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Stabilization of the $P(CF_3)_2^-$ and $P(C_6F_5)_2^-$ Ions by Coordination to Pentacarbonyl Tungsten: Structures of [18-crown-6-K]$P(CF_3)_2$, [18-crown-6-K][$W\{P(CF_3)_2\}(CO)_5$], and [18-crown-6-K][$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$]·THF

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The stabilization of the $P(CF_3)_2^-$ ion by intermediary coordination to the very weak Lewis acid acetone gives access to single crystals of [18-crown-6-K]$P(CF_3)_2$. The X-ray single crystal analysis exhibits nearly isolated $P(CF_3)_2^-$ ions with an unusually short P–C distance of 184(1) pm, which can be explained by negative hyperconjugation and is also found by quantum chemical hybrid DFT calculation. Coordination of the $P(CF_3)_2^-$ ion to pentacarbonyl tungsten has only a minor effect on electronic and geometric properties of the $P(CF_3)_2$ moiety, while a strong increase in thermal stability of the dissolved species is achieved. The hitherto unknown $P(C_6F_5)_2^-$ ion is stabilized by coordination to pentacarbonyl tungsten and isolated as a stable 18-crown-6 potassium salt, [18-crown-6-K][$W\{P(C_6F_5)_2\}(CO)_5$], which is fully characterized. The tungstate, $[W\{P(C_6F_5)_2\}(CO)_5]^-$, decomposes slowly in solution, while coordination of the phosphorus atom to a second pentacarbonyl tungsten moiety results in an enhanced thermal stability in solution. The single-crystal X-ray analysis of [18-crown-6-K][$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$]·THF exhibits a very tight arrangement of the two C_6F_5 and two $W(CO)_5$ groups around the central phosphorus atom. NMR spectroscopic investigations of the $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ ion exhibit a hindered rotation of both the C_6F_5 and $W(CO)_5$ groups in solution.

Introduction

The electronic properties of perfluoroorganyl element compounds are strongly affected by the electronic characteristics of the perfluoroorganyl groups. For example, perfluoroorganylphosphanes exhibit higher ionization energies[1] and increased Lewis acidity[2] in comparison to nonfluorinated derivatives. Depending on the strong π-acidity and weak σ-basicity of perfluoroorganylphosphanes, the electron deficit at the phosphorus atoms will be transferred to the metal atom in corresponding perfluoroorganylphosphane transition metal complexes.[3,4] For this reason, perfluoroorganylphosphane ligands are important tools to tune the Lewis acidity of transition metal complexes.[4,5] To offer this application for use in asymmetric catalysis, we are investigating different strategies for the synthesis of chiral, bidentate bis(perfluoroorganyl)phosphane derivatives. In view of this target, our work is focused on the synthesis of nucleophilic $P(CF_3)_2^-$ and $P(C_6F_5)_2^-$ synthons and the investigation of their chemical properties.

For the use of the $P(CF_3)_2^-$ ion[6] in nucleophilic substitution reactions, it is necessary to reduce the negative hyperconjugation, which is associated with a C−F activation. For this reason we synthesized different bis(trifluoromethyl)phosphanido complexes of mercury[7] and silver[8] and investigated their implementation in nucleophilic substitution reactions.

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(1) For example: Gleiter, R.; Goodmann, W. D.; Schäfer, W.; Grobe, J.; Apel, J. *Chem. Ber.* **1983**, *116*, 3745−3750. Elbel, S.; Dieck, H. T. *J. Fluorine Chem.* **1982**, *19*, 349−362.

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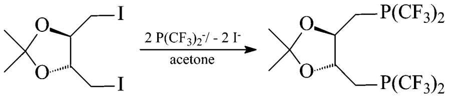
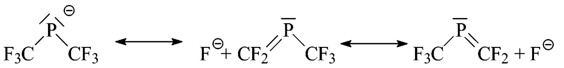
In the synthesis of the first example of a chiral bidentate bis(trifluoromethyl)phosphane derivative (**I**),[9] it was necessary to stabilize the $P(CF_3)_2^-$ ion by intermediary formation of a donor acceptor adduct, using the extremely weak Lewis acid acetone.[10]



(**I**) (1)

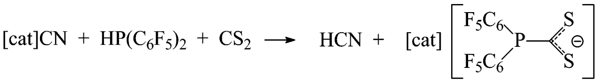
Previous hybrid density calculations of the $P(CF_3)_2^-$ ion at the B3PW91/6-311G(d) level of theory in combination with vibrational spectroscopy predicted shortened P−C and elongated C−F distances, as occurs in the case of negative hyperconjugation which can be described by the following resonance structures:[6]



(2)

To prove this prediction by single-crystal X-ray crystallography it is necessary to increase the lifetime of the $P(CF_3)_2^-$ ion in solution to obtain suitable single crystals. While the neat phosphanides $[NEt_4]P(CF_3)_2$ and [18-crown-6-K]$P(CF_3)_2$ are stable up to 140 °C, the $P(CF_3)_2^-$ ion decomposes above −30 °C in CH_2Cl_2 and THF solution.

In order to synthesize bis(pentafluorophenyl)phosphanides, we treated bis(pentafluorophenyl)phosphane, $HP(C_6F_5)_2$, with cyanide salts at low temperature. Due to the strong nucleophilicity of the $P(C_6F_5)_2^-$ ion, the anion oligomerizes even at low temperature, while the synthesis in the presence of excess CS_2 allows the isolation of the thermally sensitive CS_2 adduct (**II**).[11]



(3)

$[cat]^+ = [18\text{-crown-6-K}]^+$

(II)

A preliminary structural and density functional study on $HP(CF_3)_2$ and $HP(C_6F_5)_2$ and their pentacarbonyl tungsten complexes proves that the pentacarbonyl tungsten moiety has no major structural nor electronic influence on the $HP(CF_3)_2$ and $HP(C_6F_5)_2$ ligand in comparison to the noncoordinated phosphanes. In view of these results, we investigated the influence of pentacarbonyl tungsten moieties on coordinated $P(CF_3)_2^-$ and $P(C_6F_5)_2^-$ ions. The goal of this study is the stabilization of the $P(CF_3)_2^-$ and $P(C_6F_5)_2^-$ ions by the formation of the corresponding pentacarbonyl−phosphanido−tungstate complexes without major influence on the electronic (and that means nucleophilic) characteristics of the $P(CF_3)_2^-$ and $P(C_6F_5)_2^-$ ions.

Experimental Section

Materials and Apparatus. Chemicals were obtained from commercial sources and used without further purification. Literature methods were used for the synthesis of $HP(CF_3)_2$ and $HP(C_6F_5)_2$ and their pentacarbonyl tungsten complexes.[12] 18-Crown-6-potassium bis(trifluoromethyl)phosphanide[6] was synthesized according to the literature method.

CAUTION! The toxic compound $HP(CF_3)_2$ reacts violently with air. Solvents were purified by standard methods.[13] 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. 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 AC 200 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). Higher order NMR spectra were calculated with the program gNMR.[14] Quantum chemical hybrid density functional calculations were performed with the Gaussian 98 program package.[15]

Preparation of 18-Crown-6-potassium Pentacarbonylbis-(trifluoromethyl)phosphanidotungstate. A solution of 0.56 g (1.70 mmol) of [18-crown-6-K]CN in 5 mL of CH_2Cl_2 was added dropwise to a suspension of 0.84 g (1.70 mmol) of $[W(CO)_5PH(CF_3)_2]$ in 15 mL of CH_2Cl_2 at −78 °C. After the temperature was allowed to rise to −30 °C over 3 h, the solution was cooled to −78 °C. The product was precipitated by adding a 50 mL portion of hexane. The solution was removed via a syringe, and the solid residue was washed several times with hexane. Removal of all volatile compounds was performed during the warming up to room temperature and yielded 0.48 g (0.60 mmol, 35%) of [18-crown-6-K]$[WP(CF_3)_2(CO)_5]$ as a slightly green powder. The neat compound decomposes at 255 °C (DTA/TG). Negative ESI mass spectrum (acetone/methanol) {*m*/*z* (%) [assignment]}: 493 (10) $[WP(CF_3)_2(CO)_5]^-$; 465 (36) $[WP(CF_3)_2(CO)_4]^-$; 437 (16) $[WP(CF_3)_2(CO)_3]^-$; 409 (100) $[WP(CF_3)_2(CO)_2]^-$; 381 (13) $[WP(CF_3)_2(CO)]^-$; 353 (18) $[WP(CF_3)_2]^-$; 315 (16) $[WF(CO)_4]^-$; 287 (20) $[WF(CO)_3]^-$. Positive ESI mass spectrum (acetone) {*m*/*z* (%) [assignment]}: 303

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(100) [18-crown-6-K]. Elemental anal. (calcd for $C_{19}H_{24}F_6KO_{11}PW$): C 28.74 (28.66); H 3.10 (3.04). Infrared spectrum (cm^{-1}) (KBr pellet): 2953 w, 2919 m, 2890 m, 2861 w, 2830 w, 2799 vw, 2749 vw, 2066 m, 1971 s, 1917 vs, 1865 vs, 1829 m, 1476 w, 1454 w, 1435 vw, 1352 m, 1287 w, 1250 w, 1238 w, 1150 s, 1136 m, 1109 vs, 1067 s, 1057 s, 962 m, 837 w, 729 vw, 669 vw, 598 m, 582 m, 556 w, 529 w, 457 w, 449 w, 438 vw, 417 w. Raman (cm^{-1}): 2955 (9), 2918 (18) 2897 (17), 2879 (16), 2849 (16), 2810 (8), 2754 (3), 2729 (3), 2064 (36), 1979 (100), 1946 (13), 1915 (13), 1869 (45), 1476 (9), 1454 (3), 1410 (3), 1292 (2), 1275 (7), 1248 (5), 1146 (5), 1111 (3), 1082 (4), 1072 (3), 1061 (2), 951 (2), 872 (6), 831 (5), 729 (6), 548 (4), 532 (3), 455 (6), 438 (22), 407 (2), 475 (10), 376 (4), 289 (5), 280 (5), 255 (3), 235 (3), 201 (4), 114 (23), 93 (39). NMR data ($CDCl_3$; rt) of the [18-crown-6-K]$^+$ counterion: $\delta(^1H)$ 3.5 ppm; $\delta(^{13}C)$ 70.8 ppm. The NMR spectroscopic data of the $[WP(CF_3)_2(CO)_5]^-$ anion are summarized in Table 1. The experimental (top) and calculated (bottom) ^{31}P NMR spectrum is shown in Figure 5.

Preparation of Ethylbis(trifluoromethyl)phosphanepentacarbonyltungsten. Solutions of [18-crown-6-K]$[WP(CF_3)_2(CO)_5]$ in CH_2Cl_2 were treated at room temperature with an excess of ethyl tosylate and iodoethane, respectively. The resulting clear solutions were evaporated to dryness at 0 °C, and the product was sublimed into a stopcock vessel warming the residue up to room temperature. The product $[W(CO)_5P(CF_3)_2Et]$, a colorless solid, was identified by mass and multinuclear NMR spectroscopy. Mass spectrum (EI; 20 eV) {*m*/*z* (%) [assignment]}: 522 (100) $[W(CO)_5P(CF_3)_2Et]^+$; 494 (23) $[W(CO)_4P(CF_3)_2Et]^+$; 453 (8) $[W(CO)_5P(CF_3)Et]^+$; 438 (32) $[W(CO)_2P(CF_3)_2Et]^+$; 410 (24) $[W(CO)P(CF_3)_2Et]^+$; 382 (44) $[WP(CF_3)_2Et]^+$. NMR data of $[W(CO)_5P(CF_3)_2Et]$ (CH_2Cl_2; rt): $\delta(^{19}F)$ −60.0 ppm; $\delta(^{31}P)$ 55.8 ppm; $^1J(WP)$ 267.4 Hz; $^2J(PF)$ 69.4 Hz; $^2J(PH)$ 8.1 Hz; $^3J(PH)$ 20.4 Hz; $^3J(WF)$ 21.8 Hz. The ^{19}F NMR and ^{31}P NMR spectra are part of the Supporting Information.

Preparation of 18-Crown-6-potassium Pentacarbonylbis(pentafluorophenyl)phosphanidotungstate. A solution of 3.45 g (5.00 mmol) of $[W(CO)_5PH(C_6F_5)_2]$ in 15 mL of CH_2Cl_2 was treated dropwise with a solution of 1.65 g (5.00 mmol) of [18-crown-6-K]CN in 10 mL of CH_2Cl_2 at −50 °C. The resulting red solution was stirred for 1 h at −50 °C before the product was precipitated by the addition of 50 mL of pentane. The solution was removed via a syringe, and the solid residue was washed several times with pentane. The remaining yellow powder, 3.32 g (3.35 mmol; 67%) of [18-crown-6-K]$[W\{P(C_6F_5)_2\}(CO)_5]$, was dried in vacuo. Elemental anal. (calcd for $C_{29}H_{24}F_{10}KO_{11}PW$): C 35.02 (35.10); H 2.66 (2.44). NMR data (acetone-*d*$_6$; −40 °C) of the [18-crown-6-K]$^+$ counterion: $\delta(^1H)$ 3.6 ppm; $\delta(^{13}C)$ 71.2 ppm. The NMR spectroscopic data of the $[W[P(C_6F_5)_2\}(CO)_5]^-$ anion are summarized in Table 2. Infrared spectrum (cm^{-1}) (KBr pellet): 2903 w, 2863 vw, 2830 vw, 2054 w, 1958 m, 1906 vs, 1890 s, 1508 m, 1474 m, 1466 m, 1352 w, 1285 vw, 1252 w, 1109 s, 1072 m, 974 w, 963 m, 873 vw, 604 w, 579 w. Raman (cm^{-1}): 2951 (22), 2918 (25), 2889 (25), 2847 (21), 2810 (9), 2071 (50), 2058 (20), 1979 (100), 1948 (52), 1925 (38), 1896 (61), 1980 (61), 1641 (15); 1472 (9); 1377 (8); 1275 (8); 1246 (3); 1138 (5); 914 (4); 870 (8); 817 (14); 586 (10); 548 (4); 465 (44); 434 (42); 396 (7); 370 (5); 324 (9); 280 (5); 108 (85).

Preparation of Ethylbis(pentafluorophenyl)phosphanepentacarbonyltungsten. A THF solution of [18-crown-6-K]$[W\{P(C_6F_5)_2\}(CO)_5]$ was treated at −40 °C with an excess of iodoethane. The temperature was slowly raised to room temperature, and the product $[W(CO)_5P(C_6F_5)_2Et]$ was identified by mass and multinuclear NMR spectroscopy. The EI mass spectrum of the residue of the reaction mixture, which had been evaporated to dryness,

Table 1. NMR Spectroscopic Data for Bis(trifluoromethyl) Phosphorus Derivatives

	$\delta(^{31}P)$	$\delta(^{19}F)$	$\delta(^{13}CF_3)$	$^1J(CF)$	$^1J(PH)$	$^2J(PF)$	$^1J(PW)$	$^1J(PC)$	$^3J(FC)$	$\delta(^{13}CO)_{tr}$	$\delta(^{13}CO)_{cis}$	$^1J(W(^{13}CO)_{cis})$	$^2J(P(^{13}CO)_{tr})$	$^2J(P(^{13}CO)_{cis})$
$HP(CF_3)_2$[a]	−48.0	−47.3	128.5	317	240.7	60.6		*b*	*b*					
$P(CF_3)_2^-$ [c]	−1.9	−31.4	146.5	315.6		47.2		92.5	12.1					
$[W(CO)_5PH(CF_3)_2]$[a]	1.7	−54.9	124.5	319.1	359.5	75.9	268.8	65.8	3.5	193.7	191.4	124.5	32.3	6.7
$[W(CO)_5P(CF_3)_2]^-$ [d]	15.0	−42.8	138.2	319.2		50.1	103.1	58.9	8.2	203.6	198.9	124.7	11.5	3.4

[a] Reference 12. [b] Not observed. [c] Reference 6. [d] See Experimental Section.

exhibits characteristic fragments (EI; 20 eV) {m/z (relative intensities of the compound [$W(CO)_5PEt(C_6F_5)_2$]) [assignment]}: 718 (80) [$W(CO)_5PEt(C_6F_5)_2]^+$; 690 (90) [$W(CO)_4PEt(C_6F_5)_2]^+$; 662 (100) [$W(CO)_3PEt(C_6F_5)_2]^+$; 634 (70) [$W(CO)_2PEt(C_6F_5)_2]^+$; 606 (65) [$W(CO)PEt(C_6F_5)_2]^+$; 578 (75) [$WPEt(C_6F_5)_2]^+$; 549 (73) [$WP(C_6F_5)_2]^+$. NMR data of [$W(CO)_5P(C_6F_5)_2Et$] (THF-d_8; rt): $\delta(^{19}F_o)$ -130.5 ppm; $\delta(^{19}F_m)$ -159.6 ppm; $\delta(^{19}F_p)$ -149.0 ppm; $\delta(^{31}P)$ -12.0 ppm; $^1J(WP)$ 250.4 Hz; $^3J(PH)$ 22.9 Hz. The ^{19}F NMR and ^{31}P NMR spectra are part of the Supporting Information.

Preparation of 18-Crown-6-potassium *μ*-Bis(pentafluorophenyl)phosphanido-bispentacarbonyltungstgate. A freshly prepared solution of 1.78 g (4.5 mmol) of [$W(CO)_5THF$] in 200 mL of THF was added to a solution of 2.98 g (3.00 mmol) of [18-crown-6-K][$W\{P(C_6F_5)_2\}(CO)_5$] in 20 mL of THF at -50 °C. The solution was stirred for 6 h and allowed to reach room temperature. After evaporation of the solution to dryness in vacuo, the residue was extracted with 20 mL of THF. The solution was treated with 20 mL of diethyl ether and filtered. The solvent was removed in vacuo and the residue extracted several times with hexane to remove [$W(CO)_6$], yielding 1.96 g (1.50 mmol) of [18-crown-6-K][$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$] as a crude yellow powder. Negative ESI mass spectrum (acetone/methanol) {m/z (%) [assignment]}: 1013 (4) [$W_2(CO)_{10}\{P(C_6F_5)_2\}]^-$; 985 (12) [$W_2(CO)_9\{P(C_6F_5)_2\}]^-$; 957 (12) [$W_2(CO)_8\{P(C_6F_5)_2\}]^-$; 929 (100) [$W_2(CO)_7\{P(C_6F_5)_2\}]^-$; 901 (5) [$W_2(CO)_6\{P(C_6F_5)_2\}]^-$; 873 (6) [$W_2(CO)_5\{P(C_6F_5)_2\}]^-$; 845 (4) [$W_2(CO)_4\{P(C_6F_5)_2\}]^-$; 817 (20) [$W_2(CO)_3\{P(C_6F_5)_2\}]^-$; 689 (4) [$W(CO)_5\{P(C_6F_5)_2\}]^-$; 661 (6) [$W(CO)_4\{P(C_6F_5)_2\}]^-$. NMR data (acetone-$d_6$; rt) of the [18-crown-6-K]$^+$ counterion: $\delta(^1H)$ 3.6 ppm; $\delta(^{13}C)$ 71.2 ppm. The NMR spectroscopic data of the [$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ anion are summarized in Table 2. The temperature dependent ^{19}F NMR spectra are shown in Figure 6. The ^{31}P NMR spectrum showing tungsten satellites and tungsten satellites of the tungsten satellites is part of the Supporting Information.

Crystal Structure Determination. Crystals of [18-crown-6-K]$P(CF_3)_2$ slowly grew while diethyl ether was distilled onto an acetone solution of [18-crown-6-K]$P(CF_3)_2$ at -45 °C. Single crystals of [18-crown-6-K][$W\{P(CF_3)_2\}(CO)_5$] were obtained by the same method. Intense yellow single crystals of [18-crown-6-K][$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$]·THF were obtained by slow evaporation of a THF/hexane solution of this compound at room temperature. 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 data for [18-crown-6-K]$P(CF_3)_2$ were collected at 170 K by ω-scans in 116 frames ($0° \leq \omega \leq 180°$, $\psi = 0°$; $0° \leq \omega \leq 52°$, $\psi = 90°$; $\Delta\omega = 2°$, exposure time of 10 min) in the 2θ range of 3.8$-$70.6°. Intensity data for [18-crown-6-K][$WP(CF_3)_2(CO)_5$] were collected at 170 K by ω-scans in 108 frames ($0° \leq \omega \leq 180°$, $\psi = 0°$; $0° \leq \omega \leq 36°$, $\psi = 90°$; $\Delta\omega = 2°$, exposure time of 7 min) in the 2θ range of 2.3$-$59.5°. The intensity data for [18-crown-6-K][$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$]·THF were collected at 170 K by ω-scans in 146 frames ($0° \leq \omega \leq 180°$, $\psi = 0°$; $0° \leq \omega \leq 112°$, $\psi = 90°$; $\Delta\omega = 2°$, exposure time of 5 min) in the 2θ range of 1.9$-$54.8°. The structures were solved by direct methods SHELXS-97[16] and difference Fourier syntheses. Full matrix least squares structure refinements against $|F^2|$ were carried out using SHELXL-93.[17] H atom positions for

Table 2. NMR Spectroscopic Data for Bis(pentafluorophenyl) Phosphorus Derivatives

	$\delta(^{31}P)$	$\delta(^{19}F_o)$	$\delta(^{19}F_m)$	$\delta(^{19}F_p)$	$^1J(PH)$	$^1J(PW)$	$\delta(^{13}CO)_{tr}$	$\delta(^{13}CO)_{cis}$	$^1J(W(^{13}CO)_{tr})$	$^1J(W(^{13}CO)_{cis})$	$^2J(P(^{13}CO)_{tr})$	$^2J(P(^{13}CO)_{cis})$
$HP(C_6F_5)_2$[a]	-137.7	-128.3	-159.6	-149.3	236.5							
[$W(CO)_5PH(C_6F_5)_2$][a]	-100.1	-131.2	-160.3	-148.5	380.5	249.9	196.3	194.0	174.6	125.6	29.6	5.7
[$W(CO)_5P(C_6F_5)_2]^-$ [b]	-103.9	-127.9	-165.2	-162.7		99.5	205.2	201.6	*c*	*c*	13.9	*d*
[$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ [b]	-111.5	-125.1[e]	-163.5[e]	-159.1[e]		172.8	202.4	200.3	148.9	125.4	17.2	3

[a] Reference 12. [b] See Experimental Section. [c] Not observed. [d] Not resolved. [e] Triglyme, 90 °C.

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

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

Table 3. Crystal Data and Structure Refinement Parameters for [18-crown-6-K]$P(CF_3)_2$ (**I**), [18-crown-6-K][W{$P(CF_3)_2$}$(CO)_5$] (**II**), and [18-crown-6-K][{$W(CO)_5$}$_2${μ-$P(C_6F_5)_2$}]·THF (**III**)[a]

	I	**II**	**III**
empirical formula	$C_{14}H_{24}O_6F_6PK$	$C_{19}H_{24}O_{11}F_6PKW$	$C_{38}H_{32}O_{17}F_{10}PKW_2$
cryst syst	monoclinic	triclinic	triclinic
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 2))	$P\bar{1}$ (No. 2)
color, habit	colorless, plate	yellow, plate	yellow, polyhedron
unit cell dimens			
a [pm]	1633.5(8)	1045.0(2)	917.2(1)
b [pm]	964.1(3)	1139.8(2)	1556.0(2)
c [pm]	1370.2(6)	1318.1(3)	1700.7(2)
α [deg]		75.51(2)	81.96(1)
β [deg]	97.14(4)	70.58(1)	87.45(1)
γ [deg]		88.30(2)	75.43(1)
vol [nm^3]	2.141(2)	1.431(1)	2.326(1)
Z	4	2	2
formula mass	472.40	796.30	1388.41
ρ_{calc} [g cm^{-3}]	1.465	1.848	1.982
μ [mm^{-1}]	0.400	4.327	5.175
abs correction	numerical	numerical	numerical
transm max/min	0.9538/0.9801	0.3899/0,6868	0.3604/0.6236
θ range [deg]	2.46−23.00	1.69−26.00	1.36−27.29
total data collected	6761	11971	30062
index ranges	$-17 \leq h \leq 17$	$-13 \leq h \leq 14$	$-11 \leq h \leq 11$
	$-10 \leq k \leq 10$	$-15 \leq k \leq 15$	$-20 \leq k \leq 19$
	$-14 \leq l \leq 15$	$-17 \leq l \leq 18$	$-21 \leq l \leq 21$
unique data	1493	5445	10320
obsd data	757	3101	5988
diffractometer	STOE image plate diffraction system		
radiation	Mo Kα (graphite monochromator, $\lambda = 71.073$ pm)		
temp [K]	170(2)	170(2)	170(2)
R_{merg}	0.1413	0.0932	0.0845
R indexes	R1 = 0.0752	R1 = 0.0396	R1 = 0.0395
[$I > 2\sigma(I)$]	wR2 = 0.1428	wR2 = 0.0528	wR2 = 0.0781
R indexes	R1 = 0.1535	R1 = 0.0978	R1 = 0.0838
(all data)	wR2 = 0.1744	wR2 = 0.0679	wR2 = 0.0898
GOF (S_{obs})	0.954	0.678	0.824
GOF (S_{all})	0.954	0.641	0.824
no. of variables	177	357	599
F(000)	976	776	1336
largest diff map hole/peak [e 10^{-6} pm^{-3}]	−0.284/0.773	−1.146/0.827	−2.163/1.683

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$, $wR2 = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum w(|F_o|^2)^2]^{1/2}$, $S_2 = [\sum w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, with $w = 1/[\sigma^2(F_o)^2 + (0.0771P)^2]$ for **I**, $w = 1/[\sigma^2(F_o)^2]$ for **II**, and $w = 1/[\sigma^2(F_o)^2 + (0.0403P)^2]$ for **III**, $P = (F_o^2 + 2F_c^2)/3$. $F_c^* = kF_c[1 + 0.001|F_c|^2\lambda^3/\sin(2\theta)]^{-1/4}$.

[18-crown-6-K]$P(CF_3)_2$ were taken from the difference Fourier card at the end of the refinement. The hydrogen atoms in [18-crown-6-K][W{$P(CF_3)_2$}$(CO)_5$] and [18-crown-6-K][{$W(CO)_5$}$_2${μ-P-$(C_6F_5)_2$}]·THF were placed geometrically and held in the riding mode (except the solvent molecule in [18-crown-6-K][{$W(CO)_5$}$_2$-{μ-$P(C_6F_5)_2$}]·THF). 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 (except the C and O atoms of the solvent molecule in [18-crown-6-K][{$W(CO)_5$}$_2${μ-$P(C_6F_5)_2$}]·THF), and isotropic thermal parameters for all hydrogen atoms. Details of the refinements are given in Table 3.

Results and Discussion

To describe the bonding situation of the $P(CF_3)_2^-$ ion by single-crystal X-ray crystallography we chose a compound with weak interionic interactions, i.e., the [18-crown-6-K] salt, where the potassium cation should be shielded by the coordination of the crown ether, preventing strong interactions with the $P(CF_3)_2^-$ ion. Several attempts to obtain single crystals of [18-crown-6-K]$P(CF_3)_2$ via cooling of saturated CH_2Cl_2, $CHCl_3$, or THF solutions yielded polycrystalline material. If slow cooling rates are used, decomposition of the $P(CF_3)_2^-$ ion occurs. The slow distillation of hexane or diethyl ether onto CH_2Cl_2, $CHCl_3$, or THF solutions of the salt at −78 °C yielded also polycrystalline material, or resulted, if slow distillation rates were used, in a complete decomposition of the $P(CF_3)_2^-$ ion in solution. During our research in the synthesis of chiral bidentate bis(trifluoromethyl)phosphane derivatives, we found that acetone stabilizes the $P(CF_3)_2^-$ ion by formation of dynamic Lewis acid Lewis base adducts **III**. The intermediary formation of the adduct **III** was proven by reaction with tetrakis(trifluoromethyl)diphosphane, $(CF_3)_2PP(CF_3)_2$, yielding the novel phosphane phosphinite derivate **IV**.[10]

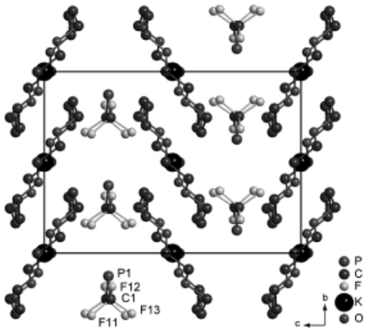
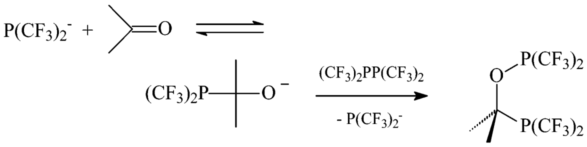


Figure 1. Unit cell packing of [18-crown-6-K]$P(CF_3)_2$ in the *b*, *c* plane showing all non-hydrogen atoms.



(III) (IV) (4)

By slow distillation of diethyl ether onto a solution of [18-crown-6-K]$P(CF_3)_2$ in acetone at −45 °C we were able to obtain colorless single crystals, suitable for single-crystal X-ray structure analysis. The compound [18-crown-6-K]P-$(CF_3)_2$ crystallizes in the monoclinic space group *C*2/*c*. The packing in the unit cell at the *b*, *c* plane is given in Figure 1. The long phosphorus potassium distance of 363.6(2) pm confirms the packing of isolated ions, as it was previously predicted by the very good agreement between calculated vibrational frequencies of a noninfluenced $P(CF_3)_2^-$ ion and the experimentally observed frequencies of the $P(CF_3)_2^-$ ion in its [18-crown-6-K] salt. The molecular structure of the $P(CF_3)_2^-$ ion is shown in Figure 2. Depending on the F12C1C1′F12′ and F11C1C1′F13′ dihedral angles of 3.3° and 5.8°, respectively, the $P(CF_3)_2^-$ is a member of the point group C_2, as predicted by density functional theory. The calculated dihedral angle of 3.7° exhibits an unexpected good agreement with the experimental values. The bond lengths and angles of the $P(CF_3)_2^-$ ion as its [18-crown-6-K] salt

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

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

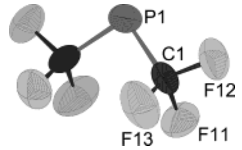

Figure 2. Molecular structure and the atom-numbering scheme of $P(CF_3)_2^-$ anion in the compound [18-crown-6-K]$P(CF_3)_2$. Probability amplitude displacement ellipsoids (50%) are shown.

Table 4. Bond Lengths (pm) and Angles (deg) of the $P(CF_3)_2^-$ Anion in the Compound [18-crown-6-K]$P(CF_3)_2$

P1−C1	184(1)	C1−F13	136(1)
C1−F12	134.5(9)	P1−K1	363.6(2)
C1−F11	135(1)		
C1−P1−C1	96.9(5)	F12−C1−P11	108.9(6)
F12−C1−F11	104.7(7)	F11−C1−P11	118.6(7)
F12−C1−F13	103.9(8)	F13−C1−P1	115.1(6)
F11−C1−F13	104.2(8)		

are summarized in Table 4. The experimental P−C distance of 184(1) pm is in reasonably good agreement with 186.1 pm obtained at the B3PW91/6-311G(3d) level of theory. HDFT calculations of the SCF_3^- ion exhibit an enhanced accuracy of the geometric parameters, if an increased set of d-polarization functions is used.[20] The same effect is observed if the geometry of the $P(CF_3)_2^-$ is optimized at the same level of theory. The resulting P−C distance of 185.4 pm is in very good agreement with the experimental value. A comparison between experimental and theoretical geometric parameters is given in Table 7, where the data of the $P(CF_3)_2^-$ are also compared with the calculated data of the neutral $HP(CF_3)_2$. The phosphorus carbon distance in $P(CF_3)_2^-$ is shortened by comparison to those in $HP(CF_3)_2$ and solid or gaseous tetrakis(trifluoromethyl)diphosphane, $(CF_3)_2PP(CF_3)_2$,[21] by 4.8, 4.1, and 5.4 pm, respectively. The shortening of the P−C distance in the $P(CF_3)_2^-$ ion is accompanied by a slight elongation of the C−F distances, which can be attributed to negative hyperconjugation or formulation of additional resonance structures, eq 2. This kind of C−F activation favors intermolecular decomposition reactions of the dissolved compound. The nature of the decomposition is not completely resolved. The novel phosphoranide, $[P(CF_3)_2F_2]^-$, is the only identified decomposition product so far.[22]

For an electronic stabilization of the $P(CF_3)_2^-$ ion, it is necessary to reduce the negative hyperconjugation. This can be achieved by reducing the electron density at the phosphorus atom. The carbon phosphorus distance in the Lewis acid Lewis base adduct $[P(CF_3)_2CS_2]^-$ is increased by around 5 pm in comparison to that in the $P(CF_3)_2^-$ ion, indicating a reduced negative hyperconjugation which is accompanied by a reduced electron density at the phosphorus atom. As a result of the reduced electron density, the CS_2 adduct $[P(CF_3)_2CS_2]^-$ exhibits a reduced reactivity as a nucleophilic $P(CF_3)_2$ group transfer reagent. While $[P(CF_3)_2CS_2]^-$ reacts with iodoethane to give $EtP(CF_3)_2$, no reaction could be observed by treatment of $[P(CF_3)_2CS_2]^-$ with ethyl tosylate.

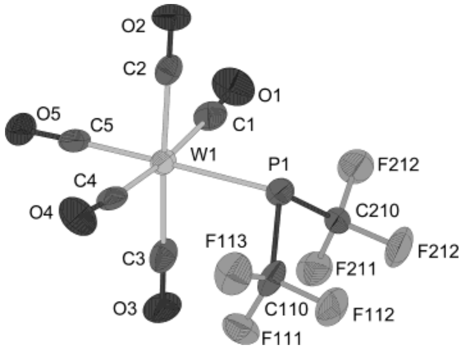

Figure 3. Molecular structure and the atom-numbering scheme of $[W\{P(CF_3)_2\}(CO)_5]^-$ in the compound [18-crown-6-K]$[W\{P(CF_3)_2\}(CO)_5]$. Probability amplitude displacement ellipsoids (50%) are shown.

To allow selective nucleophilic substitution reactions of the $P(CF_3)_2^-$ ion, a Lewis acid that stabilizes the $P(CF_3)_2^-$ ion without significant influence on the nucleophilicity of the $P(CF_3)_2$ moiety is needed. Low oxidation state transition metal phosphane complexes exhibit a σ-donation and π-back-bonding bonding dualism. The unexpected minor influence on the electronic properties of $HP(CF_3)_2$ and $HP(C_6F_5)_2$ on coordination to pentacarbonyl tungsten, which is evidenced by the small change on the ν(PH) vibrational modes, can be described by a compensation of the σ-donation with the π-back-bonding effect.

To investigate the influence on the electronic properties of the $P(CF_3)_2^-$ ion by coordination to pentacarbonyl tungsten, $[W(CO)_5PH(CF_3)_2]$ was treated with [18-crown-6-K]CN.

$$[W(CO)_5PH(CF_3)_2] + [18\text{-crown-6-K}]CN \xrightarrow[CH_2Cl_2]{} HCN + [18\text{-crown-6-K}][W\{P(CF_3)_2\}(CO)_5] \quad (5)$$

The anion $[W\{P(CF_3)_2\}(CO)_5]^-$ exhibits a remarkably increased thermal stability. Solutions of [18-crown-6-K]$[W\{P(CF_3)_2\}(CO)_5]$ in CH_2Cl_2 or acetone exhibit no sign of decomposition after 3 days at room temperature. The solid decomposes at 255 °C. Colorless crystals of [18-crown-6-K]$[W\{P(CF_3)_2\}(CO)_5]$ were obtained by distilling diethyl ether onto a solution in CH_2Cl_2 at −45 °C. The compound crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of the tungstate, $[W\{P(CF_3)_2\}(CO)_5]^-$, with approximate C_s symmetry is shown in Figure 3. Selected bond lengths and angles of the $[W\{P(CF_3)_2\}(CO)_5]^-$ ion are summarized in Table 5. A comparison of the geometric parameters of $[W(CO)_5PH(CF_3)_2]$ with the deprotonated counterpart, $[W\{P(CF_3)_2\}(CO)_5]^-$, reveals an elongation of the P−W distance by more than 15 pm, which can be attributed to a reduced π-back-bonding effect of the $P(CF_3)_2^-$ ion in comparison with $HP(CF_3)_2$. The elongation of the P−W distance is accompanied by a reduction of the magnitude of the ^1J(PW) coupling constant from 268.6 to 103.1 Hz.

As expected for the weaker π-acidic ligand, $P(CF_3)_2^-$, the highest vibrational ν(CO) valence mode of the complex

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(20) Tyrra, W.; Naumann, D.; Hoge, B.; Yagupolskii, Y. L. *J. Fluorine Chem.* **2003**, *119*, 101−107.

(21) Becker, G.; Golla, W.; Grobe, J.; Klinkhammer, K. W.; Van, D. L.; Maulitz, A. H.; Mundt, O.; Oberhammer, H.; Sachs, M. *Inorg. Chem.* **1999**, *38*, 1099−1107.

(22) Röschenthaler, G.-V.; Shyshkov, O.; Kolomeitsev, A.; Hoge, B. 16th Winter Fluorine Conference, St. Pete Beach, FL, 2003;Paper 54.

Table 5. Selected Bond Lengths (pm) and Angles (deg) of the $[W\{P(CF_3)_2\}(CO)_5]^-$ Anion in the Compound [18-crown-6-K]$[W\{P(CF_3)_2\}(CO)_5]$

W1−C5	194.2(9)	C210−F212	135.3(8)
W1−C4	201(1)	C210−F211	136(1)
W1−C2	203(1)	C210−F212	136.7(9)
W1−C3	205(1)	F112−K2	308.8(6)
W1−C1	205(1)	F212−K2	311.2(6)
W1−P1	257.9(2)	C1−O1	114(1)
P1−C210	184.4(9)	C2−O2	115(1)
P1−C110	186.0(9)	C3−O3	114(1)
C110−F112	134.4(9)	C4−O4	117(1)
C110−F111	135(1)	C5−O5	118(1)
C110−F113	136.2(9)	O5−K1	278.6(7)
C4−W1−C1	174.4(4)	C210−P1−W1	107.0(3)
C2−W1−C1	87.9(3)	C110−P1−W1	107.5(3)
C3−W1−C1	91.4(4)	F112−C110−F111	103.9(7)
C5−W1−P1	179.1(3)	F112−C110−F113	105.4(6)
C210−P1−C110	95.1(4)	F111−C110−F113	104.6(7)

Table 6. Selected Bond Lengths (pm) and Angles (deg) of the $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ Anion in the Compound [18-crown-6-K]$[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]$·THF

W1−C141	198.7(8)	W2−C211	204.0(8)
W1−C151	202.5(9)	W2−C221	204(1)
W1−C111	203.7(9)	W2−C251	205.2(9)
W1−C121	204(1)	W2−C241	205.7(8)
W1−C131	207.2(8)	W2−P1	262.9(2)
W1−P1	261.4(2)	C211−O211	113.7(9)
C111−O111	114.3(9)	C221−O221	115(1)
C121−O121	115(1)	C231−O231	115(1)
C131−O131	112.3(9)	C241−O241	112.7(9)
C141−O141	114.6(9)	C251−O251	115(1)
C151−O151	115(1)	P1−C31	186.9(8)
O151−K1	310.7(7)	P1−C21	187.5(7)
W2−C231	200.3(8)		
C151−W1−C121	176.5(3)	O131−C131−W1	177.1(7)
C111−W1−C121	90.4(3)	O141−C141−W1	178.3(7)
C141−W1−C131	91.9(3)	O151−C151−W1	176.9(6)
C151−W1−C131	88.7(3)	C151−O151−K1	143.6(6)
C111−W1−C131	177.0(3)	C221−W2−C251	174.1(3)
C121−W1−C131	92.4(3)	C231−W2−P1	175.3(3)
C141−W1−P1	176.0(2)	C31−P1−C21	97.1(3)
C151−W1−P1	92.1(2)	C31−P1−W1	119.2(2)
C111−W1−P1	89.1(2)	C21−P1−W1	99.9(2)
C121−W1−P1	91.2(2)	C31−P1−W2	101.3(2)
C131−W1−P1	91.7(2)	C21−P1−W2	119.9(2)
O111−C111−W1	175.7(7)	W1−P1−W2	118.46(7)
O121−C121−W1	175.7(7)		

Table 7. Selected Experimental and Theoretical Geometric Parameters of $P(R_F)_2^-$ $[W\{P(R_F)_2\}(CO)_5]^-$ ($R_F = CF_3$; C_6F_5), Their Protonated Derivatives, and $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ and $[\{W(CO)_5\}_2\{\mu\text{-}P(CF_3)_2\}]^-$

	X-ray	B3PW91[a]	X-ray	B3PW91[a]
	$P(CF_3)_2^-$		**$HP(CF_3)_2$**	
d(P-C)	184(1) pm	185.4 pm	-	188.8 pm
d(C-F)$_\varnothing$	135.2 pm	136.9 pm	-	134.0 pm
∠(C-P-C)	96.9(5)°	96.6°	-	99.3°
	$[W\{P(CF_3)_2\}(CO)_5]^-$		**$[W(CO)_5PH(CF_3)_2]$**	
d(P-C) {	184.4(9) pm 186.0(9) pm	188.2 pm	186.8(9) pm 188(1) pm	189.4 pm
d(C-F)$_\varnothing$	135.6 pm	135.5 pm	131.1 pm	133.6 pm
d(W-P)	257.9(2) pm	262.1 pm	242.3(2) pm	244.6 pm
d(W-C$_{tr}$)	194.2(9) pm	198.9 pm	200(1) pm	202.5 pm
d(W-C$_{cis}$)$_\varnothing$	203.5 pm	204.4 pm	203.4 pm	205.4 pm
∠(C-P-C)	95.1(4)°	96.4°	99.4(5)°	100.0°
	$P(C_6F_5)_2^-$		**$HP(C_6F_5)_2$**	
d(P-C)	-	182.2 pm	183.4 pm	184.8 pm
d(C-F)$_\varnothing$	-	134.4 pm	134.5 pm	133.1 pm
∠(C-P-C)	-	103.2°	100.1(3)°	99.9°
	$[W\{P(C_6F_5)_2\}(CO)_5]^-$		**$[W(CO)_5PH(C_6F_5)_2]$**	
d(P-C)$_\varnothing$	-	185.4 pm	182.8 pm	184.4 pm
d(C-F)$_\varnothing$	-	133.9 pm	134.3 pm	132.9 pm
d(W-P)	-	266.4 pm	247.7(1) pm	250.5 pm
d(W-C$_{tr}$)	-	198.4 pm	201.1(6) pm	201.1 pm
∠(C-P-C)	-	100.2 pm	100.4(2)°	101.9°
	$[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$		**$[\{W(CO)_5\}_2\{\mu\text{-}P(CF_3)_2\}]^-$**	
d(P-C) {	187.5(7) pm 186.9(8) pm	187.5 pm 187.4 pm	-	189.7 pm 189.7 pm
d(C-F)$_\varnothing$	134.5 pm	133.4 pm	-	134.7 pm
d(W-P) {	261.4(2) pm 262.9(2) pm	267.4 pm 267.5 pm	-	260.2 pm 260.5 pm
d(W-C$_{tr}$) {	198.7(8) pm 200.3(8) pm	198.4 pm 198.5 pm	-	199.2 pm 199.2 pm
∠(C-P-C)	97.1(3)°	98.1°	-	95.5°
∠(W-P-W)	118.46(7)	122.9°	-	124.3°

[a] For the trifluoromethyl derivatives, a 6-311G(3d) basis set was used on all nonmetal atoms, and for the pentafluorophenyl derivatives, a 6-311G(d) basis set was used on all nonmetal atoms. In the presence of a hydrogen atom, the basis set was extended by a set of p functions on the hydrogen atom. On the tungsten atom a LanL2DZ basis and ECP were used.

$[W\{P(CF_3)_2\}(CO)_5]^-$ is shifted by about 28 cm^{-1} to lower frequencies, in comparison with the protonated counterpart $[W(CO)_5PH(CF_3)_2]$, indicating an increased π-back-bonding contribution of the CO groups in the tungstate, $[W\{P(CF_3)_2\}(CO)_5]^-$. This increased π-back-bonding contribution causes a shortening of the W−C distance of the trans bonded CO group by more than 5 pm, Table 7.

Both the ^{31}P and ^{19}F NMR resonances of $[W(CO)_5PH(CF_3)_2]$ are shifted to lower field on deprotonation, which corresponds to the noncoordinated moieties, $HP(CF_3)_2$ and $P(CF_3)_2^-$, Table 1. The experimental molecular dimensions of the $[W\{P(CF_3)_2\}(CO)_5]^-$ ion are in good agreement with the optimized structure at the B3PW91/6-311G(3d) level of theory, using a LanL2DZ basis and ECP on the tungsten atom, Table 7. The following frequency analysis at the same level of theory results in a good agreement between experimental and theoretical frequencies. The calculated averaged C−O distance of 114.9 pm matches nearly exactly with the experimental value of 115.6 pm. Nevertheless the experimental anharmonic frequencies are overestimated by the calculated harmonic frequencies on the order of 80 cm^{-1}. This effect is generally observed for CO moieties: the calculated C−O distances of the noncoordinated molecules, CO, and HCO$^+$ are also close to the experimental values (in parentheses) 112.5 (112.8)[23] and 110.1 (110.7) pm,[24] respectively, while the calculated CO valence modes of 2219 and 2270 cm^{-1} overestimate the experimental values of 2143[23] and 2184 cm^{-1},[25] respectively, by around 80 wavenumbers. The remaining bond lengths of the $[W\{P(CF_3)_2\}(CO)_5]^-$ ion are overestimated by 2−4 pm, one reason why most of the calculated harmonic frequencies exhibit nearly the same value as their experimental anharmonic counterpart, without the use of a scaling factor. The approximate mode descriptions of the vibrational frequencies are presented in Table 8 and based on the corresponding calculated displacement vectors.

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Table 8. Calculated[a] Vibrational Frequencies and Observed Infrared and Raman Spectra of the $[W\{P(CF_3)_2\}(CO)_5]^-$ Ion

assignment and approx. mode descript in point group C_s		IR	Raman	calc'd[a]	[IR][b]	(Ra)[b]
$\nu_1(A')$	$\nu(CO)$	2066 m	2064 (36)	2132.2	[4.8]	(43.8)
$\nu_2(A')$		1971 s	1979(100)	2050.1	[100]	(100)
$\nu_{32}(A'')$		1917 vs	1946 (13)	2016.2	[95.2]	(0.0)
$\nu_3(A')$			1915 (13)	2015.3	[52.6]	(5.5)
$\nu_4(A')$		1865 vs	1869 (45)	1982.7	[21.1]	(50.7)
$\nu_5(A')$	$\nu(CF)$	1150 s	1146 (5)	1157.9	[14.7]	(3.2)
$\nu_{33}(A'')$		1109 vs	1111 (3)	1109.9	[4.0]	(0.0)
$\nu_6(A')$				1100.6	[12.9]	(1.2)
$\nu_7(A')$				1083.9	[0.6]	(2.1)
$\nu_{34}(A'')$		1067 s	1061 (2)	1066.2	[1.2]	(0.1)
$\nu_{35}(A'')$		1057 s		1051.3	[0.1]	(0.8)
$\nu_{36}(A'')$	$\delta_s(CF_3)$			733.9	[0.1]	(0.0)
$\nu_8(A')$	$\delta_s(CF_3)$	729 vw	729 (6)	731.0	[3.9]	(5.1)
$\nu_9(A')$		598 m		624.3	[2.3]	(0.0)
$\nu_{10}(A')$	$\delta(WCO)$	582 m		603.5	[2.5]	(0.1)
$\nu_{37}(A'')$				601.9	[0.5]	(0.0)
$\nu_{11}(A')$		556 w		556.6	[0.0]	(0.3)
$\nu_{38}(A'')$				555.5	[0.0]	(0.0)
$\nu_{12}(A')$				553.1	[0.0]	(0.3)
$\nu_{13}(A')$				548.9	[0.1]	(0.1)
$\nu_{39}(A'')$	$\delta_{as}(CF_3)$			531.8	[0.1]	(0.0)
$\nu_{14}(A')$		529 w	532 (3)	530.8	[0.0]	(0.9)
$\nu_{40}(A'')$				526.1	[0.0]	(0.0)
$\nu_{41}(A'')$	$\delta(WCO)$			502.4	[0.1]	(0.3)
$\nu_{15}(A')$	$\nu(WC)$	457 w	475 (10)	478.2	[1.4]	(12.2)
$\nu_{16}(A')$	$\nu_s(PC_2)$		455 (6)	460.9	[0.8]	(1.5)
$\nu_{42}(A'')$	$\nu_{as}(PC_2)$			455.0	[0.0]	(0.5)
$\nu_{17}(A')$	$\nu(WC_4)$		438 (22)	448.2	[0.0]	(15.1)
$\nu_{18}(A')$	$\nu(WC_4)$			440.7	[0.2]	(5.0)
$\nu_{19}(A')$	$\delta(PWC)$			426.4	[0.0]	(0.7)
$\nu_{43}(A'')$	$\delta(PWC)$	417 w		417.5	[1.7]	(0.2)
$\nu_{44}(A'')$	$\nu(WC_2)$		407 (2)	411.0	[2.0]	(0.4)
$\nu_{20}(A')$				403.9	[0.0]	(0.1)
$\nu_{45}(A'')$	$\delta(PWC)$			380.6	[0.4]	(0.0)
$\nu_{21}(A')$			376 (4)	375.3	[0.0]	(0.5)
$\nu_{22}(A')$	$\delta_{as}(CF_3)$		289 (5)	288.5	[0.0]	(0.9)
$\nu_{46}(A'')$				269.2	[0.0]	(0.3)
$\nu_{47}(A'')$			255 (3)	254.1	[0.0]	(0.2)
$\nu_{23}(A')$	$\nu(WP)$		201 (4)	192.9	[0.0]	(1.4)
$\nu_{24}(A')$				126.9	[0.0]	(0.2)
$\nu_{25}(A')$				102.3	[0.0]	(0.7)
$\nu_{48}(A'')$				100.4	[0.0]	(0.0)
$\nu_{49}(A'')$				92.5	[0.0]	(3.8)
$\nu_{26}(A')$				91.5	[0.0]	(1.0)
$\nu_{50}(A'')$				86.7	[0.0]	(3.7)
$\nu_{27}(A')$				86.4	[0.0]	(2.0)
$\nu_{28}(A')$				75.8	[0.0]	(0.3)
$\nu_{51}(A'')$				74.4	[0.0]	(0.3)
$\nu_{29}(A')$				62.9	[0.0]	(0.2)
$\nu_{52}(A'')$				57.5	[0.0]	(0.0)
$\nu_{30}(A')$				55.1	[0.0]	(0.0)
$\nu_{31}(A')$				46.9	[0.0]	(0.1)
$\nu_{53}(A'')$	$\tau(CF_3)$			38.8	[0.0]	(0.0)
$\nu_{54}(A'')$				15.1	[0.0]	(0.0)

[a] B3PW91: 6-311G(3d) basis on all nonmetallic atoms and a LanL2DZ basis and ECP on tungsten. [b] Relative intensities.

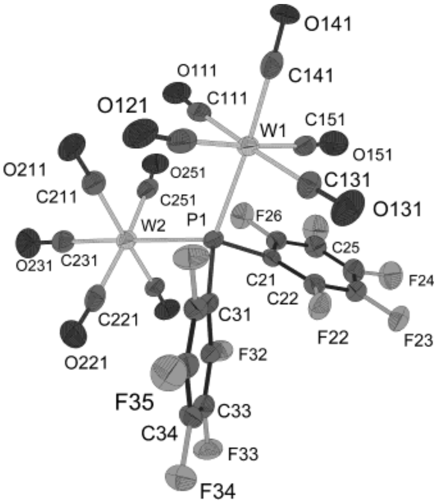
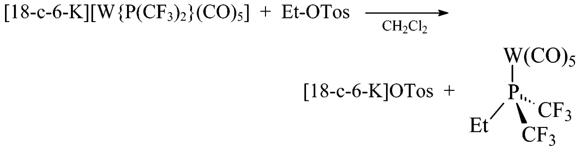


Figure 4. A central projection and the atom-numbering scheme of the anion $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ in the compound [18-crown-6-K]$[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]\cdot$THF. Probability amplitude displacement ellipsoids (50%) are shown.

The elongated W−P bond length of the $[W\{P(CF_3)_2\}(CO)_5]^-$ ion in comparison to that of the protonated derivative of about 16 pm is accompanied by a shift of the ν(W−P) valence mode by less than 10 cm^{-1} to lower frequencies. The P−C bond length of the $P(CF_3)_2^-$ ion of 184(1) pm (C_2 symmetry) is very close to the distances found in the comparable pentacarbonyl tungsten complex, $[W\{P(CF_3)_2\}(CO)_5]^-$, of 184.4(9) and 186.0(9) pm, while the adduct formation of the $P(CF_3)_2^-$ ion with CS_2 is accompanied by a P−C bond length elongation of ca. 5 pm. The fact that the P−C bond lengths of the free $P(CF_3)_2^-$ ion and the comparable pentacarbonyl tungstate complex are nearly identical indicates that the electronic properties of the $P(CF_3)_2$ unit are practically unaffected by coordination, which is also supported by the distinct nucleophilicity of the $[W\{P(CF_3)_2\}(CO)_5]^-$ ion. While the $[P(CF_3)_2CS_2]^-$ ion exhibits no reaction toward ethyl tosylate, $[W\{P(CF_3)_2\}(CO)_5]^-$ reacts smoothly with ethyl tosylate to give $[W(CO)_5PEt(CF_3)_2]$, which was identified by multinuclear NMR and mass spectroscopy.



$$[18\text{-c-6-K}][W\{P(CF_3)_2\}(CO)_5] + \text{Et-OTos} \xrightarrow[CH_2Cl_2]{} [18\text{-c-6-K}]\text{OTos} + (CO)_5W\text{-}PEt(CF_3)_2 \quad (6)$$

All attempts to synthesize a bis(pentafluorophenyl)phosphanide salt by reacting $HP(C_6F_5)_2$ with ionic cyanides at low temperature led to oligomerization of the initially formed $P(C_6F_5)_2^-$ ion. On the other hand, we succeeded in synthesizing the bis(pentafluorophenyl)phosphanide anion as the pentacarbonyl tungsten complex, $[W\{P(C_6F_5)_2\}(CO)_5]^-$. Treatment of $[W(CO)_5PH(C_6F_5)_2]$ at low temperature with [18-crown-6-K]CN yielded [18-crown-6-K]$[W\{P(C_6F_5)_2\}(CO)_5]$ as a bright yellow powder.

$$[W(CO)_5PH(C_6F_5)_2] + [18\text{-crown-6-K}]CN \xrightarrow[CH_2Cl_2]{} HCN + [18\text{-crown-6-K}][W\{P(C_6F_5)_2\}(CO)_5] \quad (7)$$

The neat compound [18-crown-6-K]$[W\{P(C_6F_5)_2\}(CO)_5]$ is stable at room temperature and can be stored for several weeks at −20 °C, while the $[W\{P(C_6F_5)_2\}(CO)_5]^-$ ion decomposes in solution even at −30 °C, yielding the same oligomeric material observed in the decomposition of the $P(C_6F_5)_2^-$ ion. The experimental ^{31}P NMR spectrum of the $[W\{P(C_6F_5)_2\}(CO)_5]^-$ ion is compared with a calculated spectrum in Figure 5. It exhibits a quintet of quintets splitting,

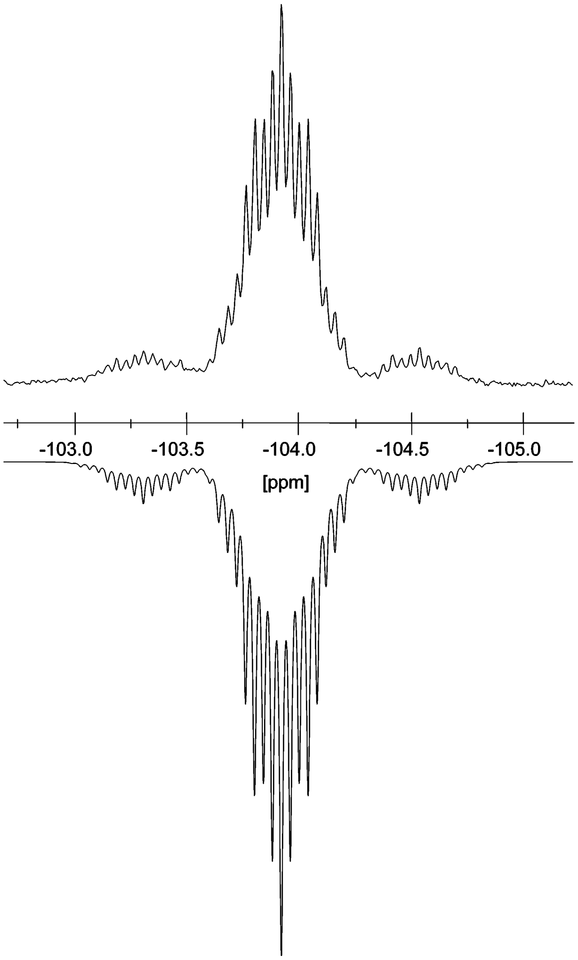
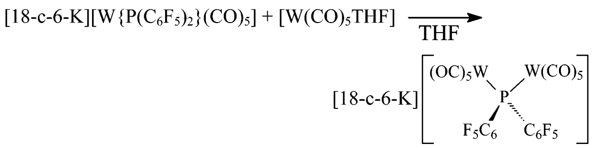


Figure 5. Experimental (top) and calculated (bottom) ^{31}P NMR spectrum of $[W\{P(C_6F_5)_2\}(CO)_5]^-$.

caused by a $^3J(PF)$ and $^4J(PF)$ coupling, surrounded by a set of tungsten satellites.

On addition of iodoethane at −40 °C, the $[W\{P(C_6F_5)_2\}(CO)_5]^-$ ion reacts in a plain reaction to give the novel compound $[W(CO)_5PEt(C_6F_5)_2]$, while the reaction with the less reactive ethyl tosylate is not selective. It was necessary to enhance the lifetime of the $[W\{P(C_6F_5)_2\}(CO)_5]^-$ ion in solution in order to obtain suitable single crystals for an X-ray structure analysis. For this purpose we reacted 18-crown-6-K][$W\{P(C_6F_5)_2\}(CO)_5$] dissolved in THF with a freshly prepared solution of $[W(CO)_5THF]$ at low temperature.



(8)

The bimetallic μ-phosphanido bridged complex, $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$, exhibits no sign of decomposition even after 1 week in solution and is stable on short contacts with air. The compound [18-crown-6-K][$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$] crystallizes in the triclinic space group $P\bar{1}$. The molecular structure of the anion, $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$, is shown in Figure 4 as a central projection. Selected bond lengths and angles of the $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ ion are summarized in Table 6. The molecular structure of the $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ ion exhibits a tight arrangement of the spatially demanding $W(CO)_5$ and C_6F_5 groups around the central phosphorus atom. As expected by this tight arrangement, the C_6F_5 as well as the $W(CO)_5$ groups show a hindered rotation in their ^{19}F and ^{13}C NMR spectra, respectively. The temperature dependent ^{19}F NMR spectra of the $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ ion are shown in Figure 6 and exhibit a splitting of the ortho fluorine nuclei of 1.1 ppm at −30 °C in THF solution, while the resonances coalesce at around 90 °C. The low-temperature ^{13}C NMR spectrum of $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ exhibits a splitting of the cis-oriented CO groups into two resonances, separated by 0.2 ppm at −40 °C. A separation of the multiplet resonances of the C_6F_5 groups could not be resolved in the ^{13}C NMR experiment. The ^{31}P NMR spectrum of the $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ ion exhibits two sets of tungsten satellites with a $^1J(WP)$ coupling constant of 172.8 Hz.

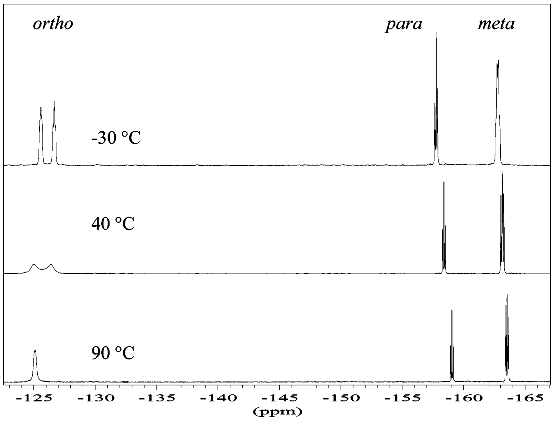


Figure 6. Temperature dependent ^{19}F NMR spectra of the $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]^-$ ion.

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Supporting Information Available: Crystallographic file in CIF format for the compounds [18-crown-6-K]$P(CF_3)_2$, [18-crown-6-K][$W\{P(CF_3)_2\}(CO)_5$], and [18-crown-6-K][[$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$]·THF. ^{19}F NMR and ^{31}P NMR spectra of $[W(CO)_5PEtR_2]$ with R = CF_3 and C_6F_5 and the ^{31}P NMR spectrum of $[\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}]$. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for the structures of [18-crown-6-K]$P(CF_3)_2$, [18-crown-6-K][$W\{P(CF_3)_2\}(CO)_5$], and [18-crown-6-K][$\{W(CO)_5\}_2\{\mu\text{-}P(C_6F_5)_2\}$]·THF reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-203184, CCDC-203185, and CCDC-203186, 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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[26] Program available at http://www.uni-koeln.de/themen/Chemie/software/g98ff/.