(15 mL) was added the ligand **1** (118 mg, 0.5 mmol) and the solution heated at 60 °C for 30 min. The resultant green-blue precipitate was filtered and recrystallized from hot ethanol to give **6** as a green microcrystalline solid (311 mg, 85%). MS (FAB, thiodiethanol): *m/e* 632 ($M^+ - ClO_4$), 533 ($M^+ - 2\ ClO_4$). Anal. Calcd for $C_{30}H_{26}Cl_2CuN_6O_8$: C, 49.1; H, 3.82; N, 11.5. Found: C, 48.9; H, 3.50; N, 11.1.

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Hexacoordinate Phosphorus. 4. Preparation and Characterization of Fluoro(pentane-2,4-dionato)(trifluoromethyl)phosphorus(V) Derivatives

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Fluoro(trifluoromethyl)phosphorus(V) derivatives with the pentane-2,4-dionato ligand (acetylacetone) of the general formula $F_{4-x}(CF_3)_xPOC(CH_3)C(H)C(CH_3)O$ (x = 1–3) and $CH_3(CF_3)_3POC(CH_3)C(H)C(CH_3)O$ have been prepared and compared to the known F_4P(acac) (i.e., x = 0). All are stable crystalline solids with a six-coordinate phosphorus geometry as illustrated by the characteristic high-field ^{31}P NMR chemical shifts and the ^{19}F and ^{31}P coupling constant patterns. The six-coordinate nature of these derivatives is further substantiated by the crystal and molecular structures of $F_2(CF_3)_2POC(CH_3)C(H)C(CH_3)O$ (III) and $F(CF_3)_3POC(CH_3)C(H)C(CH_3)O$ (IV). Crystal data for III: orthorhombic, space group *Pbca* (No. 61), a = 12.323 (4) Å, b = 22.871 (5) Å, c = 7.505 (5) Å, V = 2115 Å^3, Z = 8. Final R and R_w values for III were 0.090 and 0.105, respectively. The molecular structure of III shows that the acac ligand is essentially planar and that the two F and acac substituents lie in the same plane about the six-coordinate phosphorus atom. Crystal data for IV: monoclinic, space group $P2_1/c$ (No. 14), a = 10.218 (1) Å, b = 8.822 (3) Å, c = 13.930 (7) Å, β = 107.21 (3)°, V = 1196 Å^3, Z = 4. Final R and R_w values for IV were 0.047 and 0.070, respectively. The molecular structure of IV shows that the unique F occupies a position perpendicular to the central plane, which comprises two of the CF_3 groups and the two oxygen atoms of the acac ligand. The acac ligand is planar but is folded about the O–O axis by approximately 27° toward the unique fluorine. Infrared, mass, and ultraviolet spectra are reported for the compounds.

Introduction

We have previously described several neutral six-coordinate phosphorus(V) compounds with bidentate carbamate and thiocarbamate substituents.[1-7] Several structural characterizations have clearly demonstrated the six-coordinate geometry, expanding significantly the meager list of neutral λ^6-phosphorane structures. Herein we extend the system to include complexes of the acetylacetonate ligand, the prototypical member of which, $F_4POC(CH_3)C(H)CH_3O$, was synthesized in 1966[8] and structurally characterized in 1978.[9]

Experimental Section

All reactions were carried out in sealed tubes, and standard vacuum line techniques were employed for the manipulation of volatile materials. Diethyl ether was dried before use by distillation over $LiAlH_4$ and chloroform by distillation over P_2O_5. All of the phosphoranes used were prepared by the literature methods.[10,11] Sodium acetylacetonate was prepared from NaOH and acetylacetone in ethanol, and acetylacetone (Aldrich) was used as received. Infrared spectra were obtained as Nujol mulls of the solid samples with CsI plates on a Perkin-Elmer 457 grating spectrometer. Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 eV. NMR spectra were recorded on solutions of the compound in CD_2Cl_2 or $CDCl_3$. ^1H NMR spectra were measured on a Bruker WP-80 instrument in the continuous-wave mode, and the chemical shifts were measured relative to an external Me_4Si sample. ^{19}F and ^{31}P NMR spectra were recorded on a Bruker WP-400 spectrometer at 376.4 and 161.98 MHz, respectively. Chemical shifts were measured with respect to the heteronuclear ^2D lock signal and converted to the $CFCl_3$ scale in the case of ^{19}F and the H_3PO_4 scale in the case of ^{31}P by means of the appropriate conversion factors. Ultraviolet spectra were recorded in chloroform with a Unicam SP 1700 spectrophotometer. Chemical analyses were determined by Schwarzkopf Microanalytical Laboratory, Woodside, NY 11377.

(1) Preparation of (Pentane-2,4-dionato)tetrafluorophosphorus(V) (I). $F_4POC(CH_3)C(H)C(CH_3)O$ was prepared by the literature[8,9] method. The compound was recrystallized from $CHCl_3$; mp 82–83 °C. Anal. Calcd for $C_5H_7O_2F_4P$: C, 29.14; H, 3.42; F, 36.88; P, 15.03. Found: C, 29.39; H, 3.46; F, 36.86; P, 15.01. Principal mass spectral peaks: (*m/e* (relative intensity, percent of strongest peak) [identity]): 206 (7.5) [M]; 191 (5.5) [M − CH_3]; 147 (9.9) [$FPOC_4H_5$]; 107 (100.0) [F_4P]; 87 (7.0) [POC_3H_4]; 43 (41.1) [C_2H_3O].

(2) Preparation of (Pentane-2,4-dionato)(trifluoromethyl)trifluorophosphorus(V) (II). CF_3PF_4[10] (1.771 g, 10.01 mol) and acetylacetone (0.993 g, 9.93 mmol) were combined under vacuum with 10 mL of diethyl ether in a sealed tube. The mixture was allowed to warm very slowly (in a cold Dewar) overnight to room temperature. This reaction is exothermic. (At higher temperature CF_3PF_4 decomposes to PF_5,[10] which in turn yields F_4P(acac).) The reaction yielded a yellow Et_2O solution and a yellow oil, which was immiscible with the solution. This oil was separated from the Et_2O solution in a separatory funnel, and it was then treated with several portions of Et_2O until only a small residue of the oily material remained. All of these Et_2O aliquots were combined and the solvent removed in vacuo to leave a pale yellow oily material. Adding a few drops of CCl_4 to this material followed by cooling yielded a small amount of crystalline material. These crystals were oily and unsuitable for chemical analysis. By means of ^{19}F, ^1H, and ^{31}P NMR and UV spectra the crystalline product has however been identified as a mixture of the two structural isomers of $F_3(CF_3)POC(CH_3)C(H)C(CH_3)O$ (II). An NMR spectrum of the above reaction mixture before

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extraction showed II to be the primary component. The residual oily material that remained after the sequence of ether extractions was not II, according to NMR spectra. This and other minor species present were not identified.

(3) Preparation of (Pentane-2,4-dionato)bis(trifluoromethyl)difluorophosphorus(V) (III). $(CF_3)_2PF_3$[10] (2.690 g, 11.90 mmol) and acetylacetone (1.17 g, 11.70 mmol) were combined under vacuum with 10 mL of diethyl ether in a sealed tube. As the mixture was warmed with shaking, it became pale orange and the color intensified overnight. The solvent was removed in vacuo to leave an orange oil, which was then redissolved in a small amount of $CHCl_3$. Crystals, which formed when this solutions was cooled to ~-20 °C, were filtered off and washed with $CHCl_3$. The mother liquor plus washings were combined and reduced in volume by removal of the solvent under vacuum, and the resultant liquor was chilled in the freezer to form a second batch of crystals. Four such cycles ultimately yielded a quantity of white crystalline material, which was finally recrystallized from $CHCl_3$ to give a quantity of long colorless needles of $F_2(CF_3)_2POC(CH_3)C(H)C(CH_3)O$ (III; 1.107 g, 3.62 mmol, 31%), mp 124–125 °C. Anal. Calcd for $C_7H_7O_2F_8P$: C, 27.47; H, 2.30; F, 49.65; P, 10.12. Found: C, 27.76; H, 2.57; F, 50.76; P, 10.08. Principal mass spectral peaks (*m*/*e* (relative intensity %) [identity]): 287 (1.5) [M – F]; 237 (13.8) [M – CF_3]; 207 (10.9) [F_8PC_2]; 187 (9.5) [$F_3PO_2C_5H_7$]; 157 (26.9) [F_6PC]; 69 (24.4) [CF_3]; 43 (100.0) [C_2H_3O].

(4) Preparation of (Pentane-2,4-dionato)tris(trifluoromethyl)fluorophosphorus(V) (IV). $(CF_3)_3PF_2$[10] (4.129 g, 14.96 mmol) and acetylacetone (1.485 g, 14.85 mmol) were combined under vacuum with 10 mL of diethyl ether in a sealed tube. As the colorless liquid mixture was warmed from the frozen state to room temperature with shaking, a pale orange color developed, which intensified as the reaction proceeded at room temperature for several hours. Removing the solvent in vacuo gave an orange oil, which was redissolved in a minimum quantity of $CHCl_3$. Cooling this liquor to ca. -20 °C yielded crystalline material, which was filtered and washed with $CHCl_3$. Combining the washings with the remaining liquor, concentrating, and cooling yielded another batch of crystals. The yield of crystals from four such cycles was combined and recrystallized from $CHCl_3$ to give prismatic colorless crystals of $F(CF_3)_3POC(CH_3)C(H)C(CH_3)O$ (IV; 1.688 g, 4.74 mmol, 32%), mp 101–102 °C. Anal. Calcd for $C_8H_7O_2F_{10}P$: C, 26.98; H, 1.98; F, 53.35; P, 8.70. Found: C, 26.83; H, 1.92; F, 52.80; P, 8.70. Principal mass spectral peaks (*m*/*e* (relative intensity, %) [identity]): 337 (5.6) [M – F]; 287 (35.5) [M – CF_3]; 257 (10.0) [$F_{10}PC$]; 69 (23.3) [CF_3]; 43 (100.0) [C_2H_3O].

(5) Preparation of (Pentane-2,4-dionato)tris(trifluoromethyl)methylphosphorus(V) (V). $(CF_3)_3CH_3PCl$[11] (0.690 g, 2.40 mmol) and sodium acetylacetonate (0.294 g, 2.39 mmol) were combined in vacuo with 5 mL of diethyl ether in a sealed tube. As the mixture was warmed to room temperature with shaking, it became yellow and eventually, after overnight reaction, brown. The suspension was filtered to remove a white precipitate, and the solvent was removed in vacuo. The resulting brown powder was recrystallized from $CHCl_3$ to yield a small amount of off-white crystals identified as $CH_3(CF_3)_3POC(CH_3)C(H)C(CH_3)O$ (V), mp 41–43 °C. Anal. Calcd for $C_9H_{10}O_2F_9P$: C, 30.70; H, 2.86. Found: C, 30.87; H, 2.81%. A ^{19}F NMR spectrum of the initial reaction solution showed this compound to be the primary component. Principal mass spectral peaks (*m*/*e* (relative intensity, %) [identity]): 337 (2.6) [M – CH_3]; 283 (17.8) [M – CF_3]; 253 (71.0) [$F_9PC_4H_3$]; 203 (9.1) [$F_7PC_3H_3$]; 153 (5.1) [$F_5PC_2H_3$]; 69 (16.9) [CF_3]; 43 (100.0) [C_2H_3O].

(6) X-ray Data Collection and Structure Solution for Compounds III and IV. Clear colorless crystals of both compounds were obtained as described above. Data were collected on an Enraf-Nonius CAD4 diffractometer on which the crystals were cooled to -65 °C by using a cold air stream apparatus (F.T.S. Systems). It was extremely difficult to get crystals of suitable X-ray quality for compound III, and the crystal ultimately chosen, although the best of a large number sampled, still did not diffract X-rays well.[12] As a result the number of observed reflections was low and the final residuals were high (see Table I for crystal data and intensity collection details).

Intensity measurements were made with graphite-monochromated Mo Kα radiation. The automatic peak search and reflection indexing programs,[13] in conjunction with a cell reduction program, established the crystal systems, and the systematic absences unambiguously established the space groups[14] as *Pbca* (0*kl*, *k* odd; *h*0*l*, *l* odd; *hk*0, *h* odd) for compound III and $P2_1/c$ (*h*0*l*, *l* odd; 0*k*0, *k* odd) for compound IV. Cell constants were obtained from a least-squares refinement of the setting angles of 20 reflections having 2θ between 11 and 26° for compound III and 25 reflections having 2θ between 12 and 20° for compound IV.

Table I. Crystal Data and Details of Intensity Collection

	$F_2(CF_3)_2P(acac)$ (III)	$F(CF_3)_3P(acac)$ (IV)
mol formula	$C_7H_7F_8O_2P$	$C_8H_7F_{10}O_2P$
fw	306.09	356.10
cryst shape	plate	monoclinic prism
cryst size, mm	0.07 × 0.26 × 0.28	0.28 × 0.30 × 0.41
systematic absences	0*kl* (*k* odd), *h*0*l* (*l* odd), *hk*0 (*h* odd)	*h*0*l* (*l* odd), 0*k*0 (*k* odd)
space group	orthorhombic, *Pbca* (No. 61)	monoclinic, $P2_1/c$ (No. 14)
temp, °C	-65	-65
radiation (λ, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
unit cell parameters		
a, Å	12.323 (4)	10.218 (1)
b, Å	22.871 (5)	8.822 (3)
c, Å	7.505 (5)	13.930 (7)
β, deg		107.21 (3)
V, Å^3	2115	1199
Z	8	4
ρ_{calcd}, g cm^{-3}	1.922	1.977
linear abs coeff, μ, cm^{-1}	3.57	3.52
max 2θ reflecns collected, deg	54.00	52.00
takeoff angle, deg	3.00	3.00
detector aperture, mm	2.40 (horiz), 4.00 (vert)	2.40 (horiz), 4.00 (vert)
cryst to detector dist, mm	205	205
scan type	ω–2θ	ω–2θ
scan rate, deg min^{-1}	10.1–1.5	10.1–1.3
scan width, deg	0.80 + 0.35 tan θ	0.70 + 0.35 tan θ
total no. of reflecns collected	2666	2685
no. of indep reflecns	2302	2593
no. of observns ($I > 3\sigma(I)$)	907	2038
no. of variables	142	190
final *R*, R_w, GOF[a]	0.090, 0.105, 3.09	0.047, 0.070, 2.72

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$; GOF $= [\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$.

The intensity data were collected by using an ω–2θ scan with variable scan speeds chosen to give $\sigma(I)/I \leq 0.03$ within a time limit of 60 s in order to achieve improved counting statistics for both intense and weak reflections in a minimum time. The scan range was determined as a function of θ to compensate for the α_1–α_2 wavelength dispersion. Backgrounds for the peaks were measured by extending the scan 25% on either side of the calculated range. Two reflections were chosen as standard reflections and were remeasured every 60 min of exposure time to check on crystal and electronic stability over the course of data collection. For both compounds the standards showed variations of up to 11%; however, these variations were not uniform over the two standards collected for each compound and so no correction was applied. These fluctuations were probably due to slight crystal movement caused by the flow of cold air from the cooling apparatus.

The data were corrected for Lorentz and polarization effects[15] but not for absorption, owing to the very small linear absorption coefficients. Data were reduced in the usual manner by using a value of $p = 0.04$ to downweight intense reflections.

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(12) The X-ray crystallographic study for this molecule comprises report number SR:030122-04-85 from the Structure Determination Laboratory, Department of Chemistry, University of Alberta. See paragraph at the end of the paper regarding supplementary material.

(13) The diffractometer programs are those supplied by Enraf-Nonius for operating the CAD4F diffractometer with some local modifications and additions.

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I.

(15) The computer programs used in this analysis include the Enraf-Nonius Structure Determination Package by B. A. Frenz (*Computing in Crystallography*; Delft University Press: Delft, Holland, 1978; pp 64–71) and several locally written or modified programs.

Table II. Positional[a] and Thermal Parameters for $F_2(CF_3)_2P(acac)$ (III)

atom	*x*	*y*	*z*	*B*,[b] Å^2
P	343.6 (2)	125.6 (1)	204.6 (4)	1.90 (4)[c,d]
F(7)	414.3 (5)	89.9 (3)	349.4 (8)	2.8 (2)[c]
F(8)	281.8 (5)	161.7 (3)	355.3 (8)	2.7 (2)[c]
F(1)	169	70	80	2.5 (2)
F(2)	178.3 (9)	69.0 (5)	369 (2)	2.2 (2)
F(3)	280 (1)	10.6 (5)	213 (2)	2.7 (2)
F(4)	516.4 (9)	185.5 (5)	342 (1)	1.9 (2)
F(5)	522.1 (9)	181.3 (5)	60 (1)	2.1 (2)
F(6)	406.6 (9)	239.7 (5)	176 (1)	2.1 (2)
F(1)′[e]	143	82	143	4.7 (7)
F(2)′	218	50	385	4.9 (7)
F(3)′	272	18	127	3.8 (6)
F(1)″	150	82	309	5.4 (7)
F(2)″	279	17	294	4.2 (6)
F(3)″	204	50	51	4.2 (6)
F(4)′	544	170	283	11 (2)
F(5)′	484	196	23	3.4 (5)
F(6)′	413	234	263	3.3 (5)
F(4)″	548	166	119	5.0 (7)
F(5)″	417	230	94	6 (1)
F(6)″	476	205	356	4.9 (7)
O(1)	413.2 (5)	84.8 (4)	44.7 (9)	2.3 (2)[c]
O(2)	264.3 (5)	163.9 (3)	52.4 (9)	2.0 (2)[c]
C(1)	238.3 (8)	67.0 (5)	218 (2)	2.6 (2)[c]
C(2)	448.2 (9)	185.8 (5)	193 (2)	2.9 (3)[c]
C(3)	407.1 (9)	88.8 (5)	−132 (1)	2.1 (2)[c]
C(4)	486 (1)	52.0 (5)	−227 (2)	3.4 (3)[c]
C(5)	335 (1)	124.4 (6)	−218 (1)	2.8 (2)[c]
C(6)	264.7 (9)	161.1 (5)	−124 (1)	2.0 (2)[c]
C(7)	181.8 (7)	197.8 (4)	−209 (1)	3.0 (3)[c]

[a] Values ×10^3. [b] The equivalent isotropic thermal parameter given by $B = (8\pi^2/3)(U_{11} + U_{22} + U_{33})$. Anisotropic parameters are given in Table XI (supplementary material). [c] This atom was refined anisotropically. [d] The numbers in parentheses are estimated standard deviations in the least significant digits. Those parameters without an esd were not refined. [e] The primed and double-primed F atoms are the two additional sets of disordered CF_3 groups having minor occupancies (see Experimental Section).

Both structures were solved with MULTAN[16] (incorporating the RANTAN option for compound III). This yielded the positions of most non-hydrogen atoms; those remaining were located by the usual combination of least-squares refinement and difference Fourier techniques. In compound IV, the hydrogen atoms were located and were input to the least-squares cycles as fixed contributions in their idealized positions. These positions were obtained from the observed ones by assuming the appropriate hybridization of their attached carbon atom and using C–H distances of 0.95 Å. In compound III not all of the hydrogens were obvious and so none was included in the subsequent refinements.

Refinement was carried out with full-matrix least-squares techniques, minimizing the function $\sum w(|F_o| - |F_c|)^2$, with $w = 4F_o^2/\sigma^2(F_o^2)$. The neutral atom scattering factors[17] and the anomalous dispersion terms for all non-hydrogen atoms[18] were obtained from the usual sources. As refinement of compound III progressed, it became obvious that the two CF_3 groups were rotationally disordered such that, for each group, there was one major occupancy and two equally weighted minor occupancies. In the final model the three primary fluorine positions, on each CF_3 group, were assigned half-occupancies and were refined isotropically. The remaining six fluorine positions, corresponding to two CF_3 orientations, were assigned isotropic thermal parameters and occupancies of 0.25. These six minor positions were constrained to "ride" on the C atom of the group.

Analyses of F_o vs. F_c for both structures showed no unusual trends. The highest peak in the final difference Fourier map was 0.8 (2) e Å^{-3} for compound III and 0.4 (1) e Å^{-3} for compound IV.

The positional and isotropic thermal parameters for compounds III and IV are given in Tables II and III, respectively. Additional information is presented as supplementary material.

Results and Discussion

The (trifluoromethyl)fluorophosphoranes, except $CH_3(CF_3)_3PF$, react readily with acetylacetone at room temperature, undergoing single substitution of fluorine at the phosphorus center (eq 1) to form a hexacoordinate phosphorane with a bidentate dione ligand.

$$F_{5-x}(CF_3)_xP + H(acac) \rightarrow F_{4-x}(CF_3)_xP(acac) + HF \quad (1)$$

$$x = 0\text{–}3$$

NMR spectra of the reaction mixtures show the λ^6-phosphorane to be the primary component in all cases. The tetraalkyl derivative was prepared in almost quantitative yield (according to NMR) from $CH_3(CF_3)_3PCl$[19] and sodium acetylacetonate (Na(acac)) (eq 2), but the isolated yield was poor because of the high solubility

$$CH_3(CF_3)_3PCl + Na(acac) \rightarrow CH_3(CF_3)_3P(acac) + NaCl \quad (2)$$

Table III. Positional and Thermal Parameters for $F(CF_3)_3P(acac)$ (IV)

atom	*x*	*y*	*z*	*B*,[a] Å^2
P	0.73365 (5)[b]	0.00038 (6)	0.25619 (4)	1.52 (1)
F(1)	0.5933 (1)	0.0510 (2)	0.2776 (1)	2.17 (3)
F(2)	0.9538 (1)	0.0591 (2)	0.1874 (1)	3.08 (3)
F(3)	0.9137 (2)	−0.1782 (2)	0.1914 (1)	3.06 (3)
F(4)	1.0083 (2)	−0.0584 (2)	0.3289 (1)	3.10 (3)
F(5)	0.6476 (2)	−0.2752 (2)	0.1641 (1)	3.63 (4)
F(6)	0.6776 (2)	−0.1070 (2)	0.0627 (1)	3.08 (3)
F(7)	0.5006 (2)	−0.0953 (2)	0.1144 (1)	3.76 (4)
F(8)	0.7881 (2)	−0.1037 (2)	0.4513 (1)	3.84 (4)
F(9)	0.8341 (2)	−0.2689 (2)	0.3538 (1)	3.02 (3)
F(10)	0.6268 (2)	−0.2218 (2)	0.3454 (1)	3.57 (3)
O(1)	0.8232 (2)	0.1253 (2)	0.3499 (1)	1.98 (3)
O(2)	0.7066 (2)	0.1412 (2)	0.1637 (1)	1.81 (3)
C(1)	0.9112 (2)	−0.0472 (3)	0.2399 (2)	2.04 (4)
C(2)	0.6360 (3)	−0.1264 (3)	0.1443 (2)	2.35 (5)
C(3)	0.7484 (2)	−0.1557 (3)	0.3572 (2)	2.13 (4)
C(5)	0.8647 (3)	0.3401 (3)	0.4540 (2)	2.81 (5)
C(4)	0.7992 (2)	0.2703 (3)	0.3537 (2)	1.95 (4)
C(6)	0.7258 (2)	0.3511 (3)	0.2711 (2)	2.10 (4)
C(7)	0.6882 (2)	0.2849 (3)	0.1772 (2)	1.84 (4)
C(8)	0.6302 (3)	0.3725 (3)	0.0828 (2)	2.64 (5)
H(1)C(6)	0.700	0.453	0.279	3.11[c]
H(1)C(4)	0.843	0.445	0.452	3.81[c]
H(2)C(4)	0.830	0.291	0.502	3.81[c]
H(3)C(4)	0.961	0.328	0.472	3.81[c]
H(1)C(8)	0.585	0.460	0.097	3.63[c]
H(2)C(8)	0.701	0.402	0.055	3.63[c]
H(3)C(8)	0.566	0.310	0.036	3.63[c]

[a] The equivalent isotropic thermal parameter is given by $B = (8\pi^2/3)(U_{11}/\sin^2\beta + U_{22} + U_{33}/\sin^2\beta + 2U_{13}\cos\beta/\sin^2\beta)$. Anisotropic parameters are given in Table X (supplementary material). [b] Numbers in parentheses are estimated standard deviations in the least significant digits. [c] This atom was not refined.

of the product. Reactions of the other fluorophosphoranes with sodium acetylacetonate were complex, and only relatively low yields of the hexacoordinate species were obtained. We believe this to be due to secondary or tertiary substitution reactions, a process that cannot occur with the tetraalkyl derivative. The (pentane-2,4-dionate)phosphorus(V) compounds are all air-stable, moisture-sensitive, colorless crystalline solids with sharp melting points except for the isomeric mixture of II. Unlike the carbamato derivatives, they were insufficiently volatile for purification by sublimation but were successfully recrystallized from a variety of organic solvents.

Although there is a possibility of two isomers (Figure 1) in most cases, and three in the case of $F_2(CF_3)_2\overline{POC(CH_3)C(H)C(CH_3)O}$, all of the reactions with acetylacetone, except that involving

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(16) Main, P.; Lessinger, L.; Woofson, M. M.; Germain, G.; Declercq, J. P. *MULTAN 11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*; University of York, York, England, and University of Louvain, Louvain, Belgium, 1982.

(17) *International Tables for X-ray Crystallography*: Kynoch: Birmingham, England, 1974; Vol. IV, Table 2.2B.

(18) Reference 17, Table 2.3.1.

(19) $(CF_3)_3CH_3PF$ also reacted with sodium acetylacetonate but gave an alternative product. This reaction is still under investigation.

Table IV. Bond Distances[a]

atom 1	atom 2	dist	atom 1	atom 2	dist	atom 1	atom 2	dist
				$F_2(CF_3)_2P(acac)$ (III)				
P	F(7)	1.615 (4)[b]	O(1)	C(3)	1.328 (7)	C(2)	F(5)	1.36 (1)
P	F(8)	1.594 (4)	O(2)	C(6)	1.323 (8)	C(2)	F(6)	1.34 (1)
P	O(1)	1.745 (5)	C(1)	F(1)	1.347 (8)	C(3)	C(4)	1.47 (1)
P	O(2)	1.741 (5)	C(1)	F(2)	1.35 (1)	C(3)	C(5)	1.37 (1)
P	C(1)	1.869 (8)	C(1)	F(3)	1.39 (1)	C(5)	C(6)	1.39 (1)
P	C(2)	1.888 (8)	C(2)	F(4)	1.39 (1)	C(6)	C(7)	1.470 (9)
				$F(CF_3)_3P(acac)$ (IV)				
P	F(1)	1.612 (1)[b]	F(3)	C(1)	1.343 (2)	F(10)	C(3)	1.338 (2)
P	O(1)	1.746 (1)	F(4)	C(1)	1.343 (2)	O(1)	C(4)	1.306 (2)
P	O(2)	1.752 (1)	F(5)	C(2)	1.340 (2)	O(2)	C(7)	1.304 (2)
P	C(1)	1.940 (1)	F(6)	C(2)	1.337 (2)	C(5)	C(4)	1.493 (2)
P	C(2)	1.938 (2)	F(7)	C(2)	1.350 (2)	C(4)	C(6)	1.373 (2)
P	C(3)	1.942 (2)	F(8)	C(3)	1.334 (2)	C(6)	C(7)	1.379 (2)
F(2)	C(1)	1.339 (2)	F(9)	C(3)	1.338 (2)	C(7)	C(8)	1.489 (2)

[a] In angstroms. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

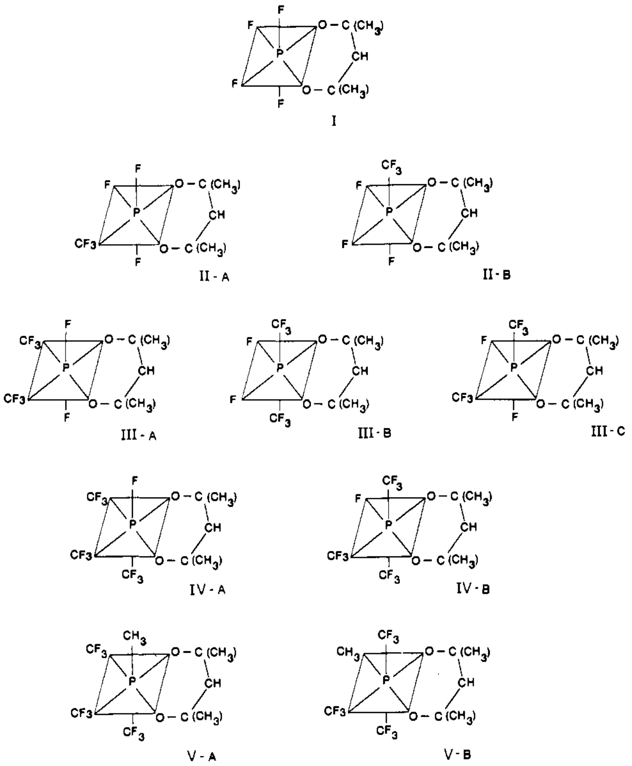


Figure 1. Isomeric structures for the various six-coordinate $F_{4-x}(CF_3)_xP(acac)$ (x = 0–3) compounds and $CH_3(CF_3)_3P(acac)$.

CF_3PF_4, gave only one specific structural isomer according to NMR spectra. The crystal and molecular structures of two compounds, $F_2(CF_3)_2P(acac)$ (III) and $F(CF_3)_3P(acac)$ (IV), were determined in order to unambiguously establish their geometries.

Structure of $F_2(CF_3)_2P(acac)$ (III). Compound III clearly has a six-coordinate geometry about phosphorus (Figure 2). The two mutually cis fluorine atoms and the acac chelate occupy "radial" positions and define the central plane of the molecule. The two CF_3 groups occupy mutually trans axial positions relative to this central plane, a position that would minimize steric interaction between the bulkiest substituents in the molecule. Relevant metrical parameters for III are given in Tables IV and V. Except for the rotational disorder exhibited by the CF_3 groups, as noted earlier, the structure is well-defined. The acac moiety and the phosphorus and fluorine atoms in the "radial" girdle are essentially coplanar; the largest deviation from the least-squares plane defined by the acac ring, the phosphorus, and two F atoms occurs for C(3) (−0.04 (1) Å). The two axial CF_3 groups are almost exactly perpendicular to the radial plane, and the small bend of the C(1)–P–C(2) axis (178.8 (4)°) tips the CF_3 groups very slightly toward the acac group. The present structure closely resembles that of $F_4P(acac)$[9] except that the P(acac) ring therein was found to have a pronounced boat shape.

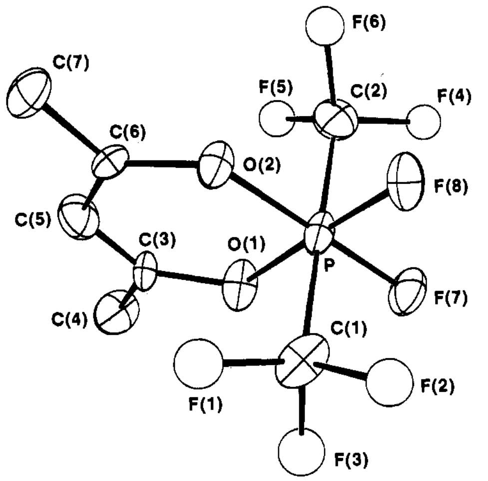


Figure 2. Perspective drawing of $F_2(CF_3)_2P(acac)$ (III) showing the numbering scheme. Thermal ellipsoids are shown at the 50% level. For the disordered CF_3 groups only the set of fluorine atoms having the major occupancy is shown.

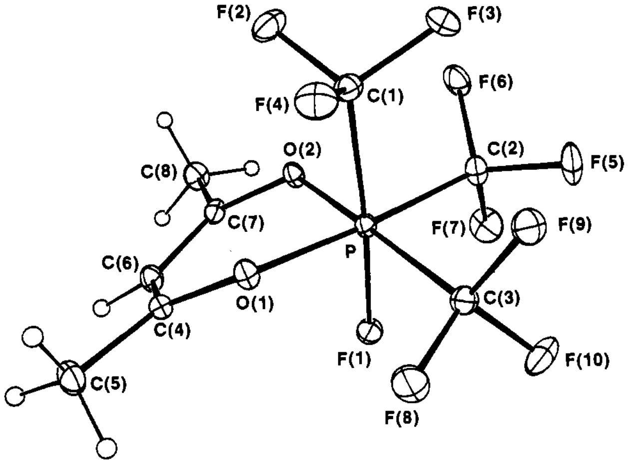


Figure 3. Perspective drawing and numbering scheme for $F(CF_3)_3P(acac)$ (IV). All atoms are shown as 50% thermal ellipsoids except hydrogens, which are drawn artifically small.

A comparison of the structures of III and $F_4P(acac)$[9] with those of analogous six-coordinate carbamates[2,5] shows that the larger P(acac) ring gives rise to an almost undistorted octahedral geometry (e.g. O(1)–P–O(2) = 95.4 (2)°) at phosphorus, whereas the rather acute carbamate O–P–O bite angles of ca. 72° produce significant distortions from idealized octahedral geometry.[2,5]

Table V. Bond Angles[a]

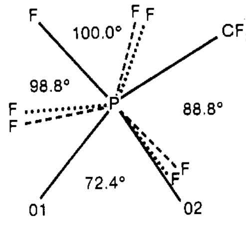
atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle	atom 1	atom 2	atom 3	angle
					$F_2(CF_3)_2P(acac)$ (III)						
F(7)	P	F(8)	92.4 (2)[b]	O(2)	P	C(1)	90.4 (3)	P	C(2)	F(5)	115.8 (6)
F(7)	P	O(1)	85.8 (2)	O(2)	P	C(2)	89.2 (3)	P	C(2)	F(6)	114.5 (5)
F(7)	P	O(2)	178.4 (3)	C(1)	P	C(2)	178.8 (4)	F(4)	C(2)	F(5)	100.6 (8)
F(7)	P	C(1)	88.6 (3)	P	O(1)	C(3)	128.4 (5)	F(4)	C(2)	F(6)	108.2 (8)
F(7)	P	C(2)	91.8 (3)	P	O(2)	C(6)	128.9 (5)	F(5)	C(2)	F(6)	104.7 (8)
F(8)	P	O(1)	178.2 (3)	P	C(1)	F(1)	111.3 (5)	O(1)	C(3)	C(4)	114.2 (6)
F(8)	P	O(2)	86.3 (2)	P	C(1)	F(2)	113.7 (6)	O(1)	C(3)	C(5)	123.2 (7)
F(8)	P	C(1)	90.1 (3)	P	C(1)	F(3)	114.3 (5)	C(4)	C(3)	C(5)	122.7 (6)
F(8)	P	C(2)	88.8 (3)	F(1)	C(1)	F(2)	107.0 (6)	C(3)	C(5)	C(6)	121.5 (6)
O(1)	P	O(2)	95.4 (2)	F(1)	C(1)	F(3)	105.1 (7)	O(2)	C(6)	C(5)	122.5 (7)
O(1)	P	C(1)	89.7 (3)	F(2)	C(1)	F(3)	104.8 (8)	O(2)	C(6)	C(7)	113.9 (6)
O(1)	P	C(2)	91.4 (3)	P	C(2)	F(4)	111.9 (6)	C(5)	C(6)	C(7)	123.5 (6)
					$F(CF_3)_3P(acac)$ (IV)						
F(1)	P	O(1)	89.15 (5)[b]	C(2)	P	C(3)	94.87 (7)	F(6)	C(2)	F(7)	105.5 (1)
F(1)	P	O(2)	89.10 (5)	P	O(1)	C(4)	125.8 (1)	P	C(3)	F(8)	113.8 (1)
F(1)	P	C(1)	174.70 (6)	P	O(2)	C(7)	125.5 (1)	P	C(3)	F(9)	114.6 (1)
F(1)	P	C(2)	91.96 (6)	P	C(1)	F(2)	112.2 (1)	P	C(3)	F(10)	110.5 (1)
F(1)	P	C(3)	86.84 (6)	P	C(1)	F(3)	113.8 (1)	F(8)	C(3)	F(9)	106.2 (1)
O(1)	P	O(2)	92.06 (5)	P	C(1)	F(4)	111.6 (1)	F(8)	C(3)	F(10)	105.8 (1)
O(1)	P	C(1)	85.55 (6)	F(2)	C(1)	F(3)	105.7 (1)	F(9)	C(3)	F(10)	105.3 (1)
O(1)	P	C(2)	175.33 (6)	F(2)	C(1)	F(4)	106.6 (1)	O(1)	C(4)	C(5)	113.9 (1)
O(1)	P	C(3)	89.72 (6)	F(3)	C(1)	F(4)	106.4 (1)	O(1)	C(4)	C(6)	122.5 (1)
O(2)	P	C(1)	90.98 (6)	P	C(2)	F(5)	114.0 (1)	C(5)	C(4)	C(6)	123.6 (2)
O(2)	P	C(2)	83.43 (6)	P	C(2)	F(6)	113.1 (1)	C(4)	C(6)	C(7)	120.3 (2)
O(2)	P	C(3)	175.55 (6)	P	C(2)	F(7)	111.6 (1)	O(2)	C(7)	C(6)	122.5 (1)
C(1)	P	C(2)	93.32 (7)	F(5)	C(2)	F(6)	105.6 (1)	O(2)	C(7)	C(8)	114.5 (1)
C(1)	P	C(3)	93.23 (7)	F(5)	C(2)	F(7)	106.4 (1)	C(6)	C(7)	C(8)	123.0 (1)

[a] In degrees. [b] Numbers in parentheses are estimated standard deviations in the least significant digits.

Structure of $F(CF_3)_3P(acac)$ (IV). The six-coordinate geometry at phosphorus is also revealed in the structure of IV (Figure 3). Metrical parameters are given in Tables IV and V. Notably, this is the first neutral λ^6-phosphorane structure in which two CF_3 groups do not occupy mutually trans axial sites; instead all three are mutually cis, in a facial arrangement. The structure of IV cannot be regarded as derived from III by simple replacement of a radial F by a CF_3 group.[2] The second anomalous feature in this structure is the unusual folding of the acac ring about the O(1)–O(2) axis; as a result the plane defined by the acac ring atoms deviates by 27° from the plane defined by P, C(2), C-(3),O(1), and O(2). It is significant also that the ring folds toward the unique axial fluorine atom. We suggest that both of these features result from crowding within compound IV.

Detailed comparison of IV with $F(CF_3)_3P(O_2CN(CH_3)_2)$[5] and $CH_3(CF_3)_3P(O_2CN(CH_3)_2)$,[2] which have a meridional arrangement of CF_3 groups, shows the carbamate structures to be almost superimposable. The orientations of the axial CF_3 groups of these carbamates (diagrammed in Figure 4) show that they are almost eclipsed to each other, and one fluorine atom on each of these CF_3 groups is almost eclipsed with O(2) of the carbamate chelate lying in the radial plane. Although this arrangement gives rise to slightly unfavorable nonbonded contacts between O(2) and these two proximal fluorines, the other two fluorines on these CF_3 groups adopt a favored, *staggered* orientation with respect to the other three radial substituents. In addition, these three radial substituents (O(1), CH_3, CF_3 or O(1), F, CF_3 on the respective carbamate compounds) are spread apart (angles at phosphorus are about 100°), further minimizing contacts of the radial substituents with fluorine atoms in the axial CF_3 groups. This relationship arises because of the small bite angle of the carbamate group and the relatively small angle (ca. 88°) between the radial CF_3 groups and the chelate. This orientation of the radial CF_3 group means that one C–F bond is eclipsed with the other radial group (F or CH_3), and this aspect has important implications regarding the difference between compound IV and the carbamates.

Replacing the carbamate group by acac provides a ligand with a larger bite angle (95°). As a result the projections of the F–C–F angles of two axial CF_3 groups (for the isomeric structure IVB) onto the O–P–O angle show greater interference, with presumably increased repulsive interactions between these moieties. In addition, less room is available for the spreading of the radial groups, so unfavorable contacts between the axial CF_3 groups and the radial substituents therefore become more severe. The influence of the radial CF_3 group becomes extremely important, since in order to remain staggered with respect to the axial groups one of its C–F bonds must be eclipsed with one of the radial groups (as observed in the carbamate structures[2,5]). The constricted radial plane makes this contact highly unfavorable, and the more favorable facial arrangement of structure IVA results. Furthermore, folding of the acac ligand bends this group away from the bulky



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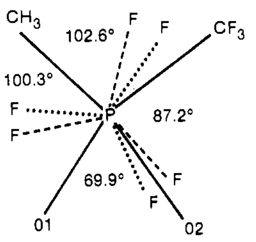

B

Figure 4. Projections of the axial CF_3 groups onto the radial planes in $F(CF_3)_3P(O_2CN(CH_3)_2)$ (A) and $CH_3(CF_3)_3P(O_2CN(CH_3)_2)$ (B). The dashed lines correspond to the C–F bonds above the radial plane, and the dotted lines correspond to the C–F bonds below this plane. The angles shown are those between adjacent radial substituents.

Table VI. Bond Distances (Å) in Phosphorus(V) Acetylacetonates and Carbamates

	P–F		P–O	P–CF_3		ref
	rad	ax		rad	ax	
$F_4P(acac)$[a] (I)	1.568 1.572	1.574 1.580	1.715 1.720	...	...	9
	1.568 1.576	1.570 1.588	1.723 1.719	...	...	
$F_2(CF_3)_2P(acac)$ (III)	1.615 (4)	...	1.741 (5)	...	1.869(8)	this work
	1.594 (4)	1.745 (5)	1.745 (5)	...	1.888 (8)	
$F(CF_3)_3P(acac)$ (IV)	...	1.612 (1)	1.752 (1)	1.938 (2)	1.940 (1)	this work
			1.746 (1)	1.942 (2)	...	
$F(CF_3)_3P(O_2CNMe_2)$	1.590 (3)	...	1.832 (3)	1.904 (5)	1.911 (5)	5
			1.778 (3)	...	1.926 (6)	
$CH_3(CF_3)_3P(O_2CNMe_2)$	...	...	1.808 (5)	1.930 (9)	1.944 (9)	2
			1.901 (5)		1.960 (9)	

[a] Standard deviations in the P–F and P–O bond lengths of $F_4P(acac)$ are 0.002.

Table VII. NMR Parameters for (Pentane-2,4-dionato)phosphorus(V) Compounds

				coupling constants, Hz			
	^1H,[c] τ	^{19}F,[d] ϕ	$^{31}P\{^1H\}$,[e] σ	$^1J_{PF}$	$^2J_{PF}$	others	
I[a]	2.3[f]	−69.0[g] (2)[h]	−148.7[i]	756.5 (rad)[j]		$^2J_{FF} = 58.5$	$^4J_{PH} = 2.0$
	6.1	−50.5[g] (2)		819.0 (ax)[j]		$^2J_{FF} = 58.5$	
IIA[b] (major)	2.5	−79.7[k] (1)	−151.7[k]	883.9 (rad)		$^2J_{FF} = 53.8$	$^3J_{FF} = 13.1$
	6.6	−70.1[l] (3)			143.4	$^3J_{FF} = 13.0$	$^3J_{FF} = 13.0$
		−59.1[m] (2)		930.2 (ax)		$^2J_{FF} = 53.8$	$^3J_{FF} = 13.0$
IIB[b] (minor)	2.5	−75.3[m] (2)	−151.0[k]	896.5 (rad)		$^2J_{FF} = 61.3$	$^3J_{FF} = 14.4$
	6.5	−70.5[l] (3)			147.8	$^3J_{FF} = 14.4$	$^3J_{FF} = 3.0$
		−64.4[k] (1)		830.0 (ax)		$^2J_{FF} = 61.5$	$^3J_{FF} = 3.0$
III[b]	2.3	−77.3[n] (2)	−151.2[o]	987.0 (rad)		$^3J_{FF} = 15.0$	
	6.0	−68.8[g] (6)			163.4	$^3J_{FF} = 15.0$	
IV[a]	2.4	−64.0[p] (1)	−158.4[q]	890.6 (ax)		$^3J_{FF} = 7.6$	$^3J_{FF} = 13.8$
	6.2	−60.8[r] (3)			94.0 (ax)	$^3J_{FF} = 7.6$	$^4J_{FF} = 9.9$
		−59.2[m] (6)			95.3 (rad)	$^3J_{FF} = 13.8$	$^4J_{FF} = 9.9$
V[a]	1.6[f]	−60.3[n] (3)	−147.8[s]	...	63.9 (rad)	$^2J_{PH} = 8.0$	$^4J_{FF} = 11.1$, $^4J_{PH} = 2.0$
	2.2[f]	−59.4[t] (6)			94.7 (ax)	$^4J_{FF} = 11.1$	
	5.9						

[a] In CD_2Cl_2. [b] In $CDCl_3$. [c] Relative to Me_4Si ($\tau = 10.0$). [d] Relative to $CFCl_3$ (negative values indicate shift to high field of standard). [e] Relative to 85% H_3PO_4 (negative values indicate shift to high field of standard). [f] Doublet. [g] Doublet of triplets. [h] Relative intensity. [i] Triplet of triplets. [j] Position of substituent: rad = coplanar with O atoms of acac substituent; ax = perpendicular to plane containing O atoms of acac. [k] Doublet of triplets of quartets. [l] Doublet of doublets of triplets. [m] Doublet of doublets of quartets. [n] Doublet of septets. [o] Triplet of septets. [p] Doublet of septets of quartets. [q] Doublet of decets (accidental degeneracy of $^2J_{PF}$). [r] Doublet of doublets of septets. [s] Septet of quartets. [t] Doublet of quartets.

CF_3 group toward the smaller F atom, creating additional space for the single axial CF_3 group. Finally, the axial CF_3 groups bends slightly toward the acac group, further reducing contacts with the two radial CF_3 groups. The resultant structure can be seen to provide minimal intramolecular interactions.

The acac group in IV is essentially planar apart from a slight boatlike bending of C(6) (−0.143 (2) Å from the plane). In spite of the folding of the acac group, all parameters within this ring resemble those in III and in $F_4P(acac)$.[9] The O–P–O angles within these acac compounds are much larger than those displayed by the carbamates (ca. 72°). This ring strain in carbamates may account for the tendency of these compounds to display fluxionality through formation of λ^5-phosphoranes with a monodentate ligand.

Comparison of Radial Bond Lengths in Hypervalent Phosphorus Compounds. Selected bond lengths of five formal (12-P-6) systems are given in Table VI. In the acetylacetonate series the P–F and P–O distances are somewhat longer in the CF_3 substituted compounds as compared to those in the fully fluorinated molecule (I). The lower electronegativity of CF_3 vs. F suggests that increasing CF_3 substitution decreases the Lewis acid strength of the phosphorus atom, resulting in a general weakening of bonding. There appears to be no significant difference between the axial and radial P–F bonds in this series. The longer average radial P–F distance in III vs. that in I parallels the longer P–O distances in IV and can be attributed to the weaker acid strength of phosphorus in IV. The P–O bond lengths in the carbamate derivatives average 1.81 (4) Å[20] in $F(CF_3)_3P(O_2CN(CH_3)_2)$ and 1.85 (7) Å in $CH_3(CF_3)_3P(O_2CN(CH_3)_2)$; both are substantially longer than those in the acetylacetonate derivatives. Presumably this weaker bonding is due to the greater ring strain of the carbamato ligand. The only P–F distance available in the carbamate series is that for $F(CF_3)_3P(O_2CN(CH_3)_2)$ in which the F atom is radially bound. This distance is a little shorter than the axial F in IVA, but it is difficult to attribute this difference to axial vs. radial location since the lengthening of the P–O bonds and the concomitant weakening of this interaction may also be responsible. There is also some variation in the P–C distances involving the CF_3 groups, and it appears that this variation is primarily steric in origin. In general the more crowded molecules show larger P–CF_3 distances. $F(CF_3)_3P(O_2CN(CH_3)_2)$ displays shorter P–C distances than those in the more crowded $F(CF_3)_3P(acac)$ molecule (vide supra), whereas the P–C distances in $F(CF_3)_3P(acac)$ and $CH_3(CF_3)_3P(O_2CN(CH_3)_2)$ are very similar.

None of the structural differences between these molecular structures can be attributed to significant axial/radial bonding differences, and this is further supported by the pattern of $^1J_{PF}$ values (vide infra).

Nuclear Magnetic Resonance Spectra. In contrast to the case for the carbamates[1-5] the acetylacetonates are not fluxional, so all of the parameters have been obtained from normal-temperature spectra. All patterns are consistent with the geometrical structures proposed, and all spectra are first order. Notably all of these compounds exhibit high-field ^{31}P NMR chemical shifts that we associate with the six-coordinate geometry. NMR spectral parameters are given in Table VII.

The simplest spectra are those shown by III. The high-field chemical shift of the directly bound fluorine is reminiscent of the trend shown by the carbamates[1-5] and is in accord with the suggestion of Sheldrick et al.[9] that radial fluorines (i.e., the fluorine atoms that are coplanar with the chelate ligand) have high-field shifts. This assignment is strongly supported by the solid-state

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[20] The esd quoted for an average value is the larger of either the standard deviation of the mean or an individual measurement.

crystal structure result, but of course there is an implicit assumption that the solid-state and solution-state structures are the same. The spectrum could be equally well assigned if the high-field chemical shift were not uniquely associated with radial positioning. Although this compound could be a fluxional mixture of IIIA and IIIB, we think fluxionality is unlikely in this sytem because the related molecules do not show any evidence for such behavior. The simplicity of the spectrum rules out IIIC, which would likely be second order.

Assuming that the solid-state structure IVA prevails in solution, the NMR spectral parameters can be easily assigned. Notably the unique fluorine has a relatively low ^{19}F chemical shift, −64.0 ppm, implying an axial position as is indicted by the crystal structure. The two CF_3 environments are clearly distinguishable with an expected 2:1 relative intensity ratio. The chemical shift and coupling constant difference between the CF_3 types is small, but the relative intensity and coupling constant patterns indicate clearly that the axial CF_3 has the higher field shift and the smaller $^2J_{PF}$ value.

The NMR spectra of II clearly show that isomers IIA and IIB are both present in 2:1 relative proportions. The assignment of the spectra is based on the association of high-field ^{19}F shifts with the radial directly bound fluorine atoms. The major isomer therefore has structure IIA with one radial F atom at −79.7 ppm, and the minor isomer has structure IIB with two radial F atoms at −75.3 ppm. The relative proportions of major/minor isomers is the reverse to that which exists for the carbamate analogue. It may be significant that for these acetylacetonates the major isomeric component of the system $F_3(CF_3)P(acac)$ is the isomer with two axial F atoms *and* the only form of $F(CF_3)_3P(acac)$ is that with an axial F. In contrast, the only isomer of $F(CF_3)_3PO_2CN(CH_3)_2$ found is that with a *radial* F atom and the major isomer of $F_3(CF_3)PO_2CN(CH_3)_2$ is apparently that with two *radial* F atoms. The pattern suggests that acetylacetonate derivatives prefer axial substitution and carbamates prefer radial substitution of fluorine, possibly the ultimate effect of the crowding discussed above. As a result the behavior of the $F_2(CF_3)_2PL$ systems (L = O_2CNMe_2 or acac) seems to be anomalous in apparently having the same structure for both ligands; however, it should be recalled from the structural discussion that this substitution pattern is consistent with steric arguments, with the bulkier CF_3 groups occupying the sterically favored positions, which can be but are not necessarily the same in the carbamate and acac species (vide supra).

Another notable feature of the CF_3 portion of the spectra of II–IV is the lack of contrast between radial and axisl $^2J_{PF}$ values and the corresponding ^{19}F chemical shifts. In contrast $^2J_{PF}$ values for radial CF_3 in the carbamate[5] groups were apparently significantly smaller than axial values.

The existence of two CF_3 environments in V is clearly visible in the shift and coupling constant patterns, and the spectra also show the appropriate 2:1 relative intensity ratio expected for either possible static structure. This is the only acac derivative that is seen to display demonstrably different axial/radial $^2J_{PF}$ values for its CF_3 groups. We speculate that structure VB may be the most probable isomeric form on the basis of associating the large value of $^2J_{PF}$ (with a total relative intensity of 2 units) with the axial CF_3 groups in parallel to the behavior of the carbamates.[5]

In general cis $^3J_{FF}$ values are in the range of 15 Hz whereas trans values are significantly smaller in parallel to the case of carbamates.[5] In IV $^3J_{FF}$(trans) is half the value of $^3J_{FF}$(cis) while in IIB the effect is more pronounced and the trans value is 3.0 Hz.

Directly bound fluorines in both acac and carbamate systems, which have high-field NMR chemical shifts, show a generally consistent trend for *major* isomers: $^1J_{PF}$(axial) is larger than $^1J_{PF}$(radial). Also, in both systems the minor isomers violate this trend: $^1J_{PF}(\text{radial}) \geq {}^1J_{PF}(\text{axial})$.

The ^1H NMR spectra (Table VII) of all of the (pentane-2,4-dionato)phosphorus(V) compounds show two signals associated with the chelate, with a 6:1 integration ratio. The larger signal corresponds to the equivalent methyl groups, and in two cases this is split by weak coupling to the phosphorus. In the asymmetric frameworks these methyl groups do not show asymmetry. The unique proton is responsible for the other signal. This proton shows no coupling characteristics, contrary to the first NMR reports[8,9] for I.

Table VIII. Infrared Spectra of (Pentane-2,4-dionato)phosphorus(V) Compounds

I	III	IV	V	assignt
1543 s, br	1540 s, br	1555 s, br	1548 s, br	$\nu_{C=O}$, $\nu_{C=C}$
1350 s, sh	1327 m	1331 s	1344 s, br	
			1320 s, sh	
	1215 s	1210 s		
	1200 m, sh	1165 s	1191 s	ν_{C-F}
	1140 s, br		1178 s	
			1142 s	
		1105 m, br	1108 s, br	
1051 m	1039 m			
1023 m	1019 m	1030 m	1030 m, br	ν_{P-O-C}
960 m	955 m	971 m		
		942 m	934 m	
880 s, br			898 m, sh	
840 s, br	824 m	824 m	805 m	
795 s, br	775 s, sh	779 s		ν_{P-F}
	760 s	745 m		
722 m	733 s	716 s		
			719 w, sh	
			700 s	
654 m	655 s		650 m	
	605 s	598 s		
553 s	565 m	561 w	569 s	
535 s		530 m		
500 m	496 s	509 w	506 s, br	
448 w	461 m	482 w	458 m	
423 vw		451 m	395 w	

[a] Abbreviations: s = strong; sh = shoulder; br = broad; m = medium; w = weak; v = very.

Table IX. Ultraviolet Spectra of (Pentane-2,4-dionato)phosphorus(V) Compounds

	λ_{max}, nm	ϵ, M^{-1}		λ_{max}, nm	ϵ, M^{-1}
I	292	15 000	IV	302	12 800
II	294	*a*	V	277	*a*
III	310	11 000			

[a] Not measured.

Infrared Spectral Properties. Infrared spectra data for complexes I, III, IV, and V are presented in Table VIII. The 1300–1600-cm^{-1} regions of the infrared spectra of the (pentane-2,4-dionato)phosphorus(V) compounds are all very similar, and by comparison to spectra of analogous metal complexes,[21–23] assignment of these bands to C=O and C=C stretching vibrations of the chelate seems reasonable. The strong bands observed between 1100 and 1200 cm^{-1} can be assigned to C–F stretching modes,[24–26] an assignment that is confirmed by the absence of these bands in the spectrum of $F_4\overline{POC(CH_3)C(H)C(CH_3)O}$. In a similar manner, the strong bands between 700 and 800 cm^{-1} are assigned to P–F stretches;[11,27] no bands are observed in this region of the spectrum of $(CF_3)_3CH_3\overline{POC(CH_3)C(H)C(CH_3)O}$, but in this region CF_3 deformations are also possible. Because the rigid six-membered ring, made up of the chelate and the phosphorus center, is unique, it is difficult to establish the bands arising from P–OC units with any certainty. Comparison with the spectra of the carbamato derivatives[2] and methoxyphosphoranes[11] suggests

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that the bands between 850 and 1100 cm^{-1} may be tentatively assigned to stretching vibrations of this portion of the molecules.

Ultraviolet Spectra. Ultraviolet spectral data for the (pentane-2,4-dionato)phosphorus(V) compounds are presented in Table IX. All of the complexes show a strong single absorption between 270 and 310 nm, which appears to relate to the characteristic strong band of the $\pi-\pi^*$ electronic transition[27,28] of the free pentane-2,4-dione at 275 nm. There are no direct parallels with metal complexes because most such systems have several pentane-2,4-dionato chelates with a resultant splitting of the π levels of the ligand. The range of transition energies demonstrated by the series can be attributed to the electrostatic effects of the other ligands on the phosphorus, which suggests some involvement of phosphorus d orbitals with the π structure of the chelate. The π HOMO and π^* LUMO can only experience such effects via interaction with the empty d_{xz} and d_{yz} orbitals of the phosphorus. There is no obvious trend to the observed energies throughout the series, but it is notable that there seems to be a regular trend of increasing λ_{max} from $F_4P(acac)$ to $F_2(CF_3)_2P(acac)$ (i.e., with increasing CF_3 substitution) that is broken by $F(CF_3)_3P(acac)$. As shown by the crystal structure, this molecule exhibits a rather unusual bending of the acac ligand, which may account for the anomaly. The fact that anomalous behavior is exhibited by the visible spectrum in solution may indicate that the bending of the substituent persists in solution and is a molecular effect rather than a crystal-packing effect.

Mass Spectra. The major mass spectral peaks observed for the (pentane-2,4-dionato)phosphorus(V) compounds (except the isomeric mixture of II) are given in the Experimental Section. $F_4\overline{POC(CH_3)C(H)C(CH_3)O}$ is the only member of the series that exhibits a parent ion, and it is further unique in showing the F_4P^+ ion as the most intense in the spectrum. In common with the case for five-coordinate phosphoranes[29] and the hexacoordinate carbamates,[2] the trifluoromethyl derivatives do not show a parent ion. In these cases the most intense peak is *m/e* 43, which corresponds to CH_3CO, a fragment of the chelate. As in the carbamato derivatives, the P–O bond is quite robust and many of the fragments can be identified as due to loss of only one CF_3 or F ligand from the parent molecule. In all cases a phosphonium ion is observed resulting from loss of the chelate.

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Supplementary Material Available: Listings of anisotropic thermal parameters and least-squares planes (6 pages); tables of calculated and observed structure factors (23 pages). Ordering information is given on any current masthead page.

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Structure and Electrochemical Properties of Antiferromagnetically Coupled Binuclear Hydroxo-Bridged Copper(II) Complexes with Pyridazine and Phthalazine Ligands. Crystal and Molecular Structures of [μ-3,6-Bis(1-pyrazolyl)pyridazine-N^2,μ-N^3,μ-N^4,N^5](μ-hydroxo)trichloroaquodicopper(II)–0.8-Water, $Cu_2C_{10}H_{11}Cl_3N_6O_2 \cdot 0.8H_2O$, [$\mu$-3,6-Bis(1-pyrazolyl)pyridazine-N^2,μ-N^3,μ-N^4,N^5](μ-hydroxo)tribromoaquodicopper(II)–0.6-Water, $Cu_2C_{10}H_{11}Br_3N_6O_2 \cdot 0.6H_2O$, and [$\mu$-1,4-Bis(1-methyl-2-imidazolyl)phthalazine](μ-hydroxo)tribromoaquodicopper(II)–Water, $Cu_2C_{16}H_{17}Br_3N_6O_3 \cdot H_2O$

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The ligands 3,6-bis(1-pyrazolyl)pyridazine (PPD) and 1,4-bis(1-methyl-2-imidazolyl)phthalazine (MIP) form binuclear copper(II) complexes in which the square-pyramidal metal centers are bridged by a hydroxide and a diazine group (N-N). Large Cu–Cu separations (3.41–3.46 Å) and Cu–O(H)–Cu bridge angles (116–125°) are observed, and the complexes exhibit very low room-temperature magnetic moments indicative of strong spin exchange. The crystal and molecular structures of $[Cu_2(PPD)(OH)Cl_3(H_2O)] \cdot 0.8H_2O$ (I), $[Cu_2(PPD)(OH)Br_3(H_2O)] \cdot 0.6H_2O$ (II), and $[Cu_2(MIP)(OH)Br_3(H_2O)] \cdot H_2O$ (III) are reported. I crystallized in the triclinic system, space group $P\bar{1}$, with $a = 7.6810$ (6) Å, $b = 9.9823$ (6) Å, $c = 10.7380$ (9) Å, $\alpha = 96.83$ (1)°, $\beta = 93.28$ (1)°, $\gamma = 91.50$ (1)°, and two formula units per unit cell. II is isostructural with I. III crystallized in the monoclinic system, space group $P2_1/n$, with $a = 10.175$ (7) Å, $b = 21.478$ (5) Å, $c = 10.198$ (8) Å, $\beta = 97.41$ (2)°, and four formula units per unit cell. Refinement by full-matrix least squares gave final residuals of $R = 0.037$ and $R_w = 0.030$ for I, $R = 0.040$ and $R_w = 0.028$ for II, and $R = 0.043$ and $R_w = 0.033$ for III. Cyclic voltammetry in DMF (glassy carbon electrode) shows single essentially nonreversible redox waves at positive potentials ($E_{1/2} = 0.41$–0.47 V vs. SCE) associated with two-electron reduction.

Introduction

Binuclear, hydroxide-bridged copper(II) complexes of tetradentate (N_4) phthalazine and pyridazine ligands have copper–copper separations in the range 3.0–3.5 Å and Cu–O(H)–Cu bridge angles in the range 100–127°.[2-11] Variable-temperature magnetic studies have shown that strong antiferromagnetic cou-

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