(d, $J_{CH} = 149$ Hz, $J_{CP} = 2.9$ Hz, $H_2C\overset{-}{\cdot\cdot}\mathit{C}H\overset{-}{\cdot\cdot}CHCH_2$), 117.6 (d, $J_{CH} = 141$ Hz, $H_2C\overset{-}{\cdot\cdot}CH\overset{-}{\cdot\cdot}\mathit{C}HCH_2$), 66.4 (dd, AB, $J_{CH} = 146.5$ and 145.5 Hz, $J_{CP} = 3.9$ Hz, $H_2\mathit{C}\overset{-}{\cdot\cdot}CH\overset{-}{\cdot\cdot}CHCH_2$), 41.0 (t, $J_{CH} = 133$ Hz, $H_2C\overset{-}{\cdot\cdot}CH\overset{-}{\cdot\cdot}CH\mathit{C}H_2$), 17.3 (dt, $J_{CH} = 135$ Hz, $J_{CP} = 13.7$ Hz, $P\mathit{C}H_2CH_3$), 7.73 (dq, $J_{CH} = 129$ Hz, $J_{CP} = 1.9$ Hz, $PCH_2\mathit{C}H_3$). The minor isomer has analogous $C_8H_{14}$ peaks at 144.5, 109.4, 68.7, and 38.8 ppm. $^{31}P\{^1H\}$ NMR of $ZrCl_2(C_8H_{12})(PEt_3)$ ($C_6D_6$): $\delta$ −2.27 (s). IR (Nujol): 1530 cm$^{-1}$ (br, m) ($\nu_{C\overset{-}{\cdot\cdot}C\overset{-}{\cdot\cdot}C}$).

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**Registry No.** $[ZrCl_3(PBu_3)_2]_2$, 77061-29-1; $[ZrCl_3(PPr_3)_2]_2$, 77061-30-4; $[ZrCl_3(PEt_3)_2]_2$, 77061-31-5; $[ZrCl_3(PBu_3)_2]_2(CH_2CH_2)$, 77061-32-6; $[ZrCl_3(PEt_3)_2]_2(CH_2CHCH_3)$, 77061-33-7; $ZrCl_2(C_8H_{12})(PEt_3)$, 77061-34-8; $ZrCl_4(PEt_3)_2$, 77061-35-9; $ZrCpCl_3(PEt_3)_2$, 77061-36-0; $C_2H_4$, 74-85-1; $MeCH{=}CH_2$, 115-07-1; $C_4H_6$, 106-99-0; TlCp, 34822-90-7.

**Supplementary Material Available:** Listings of anisotropic thermal parameters for nonhydrogen atoms of $[ZrCl_3(PBu_3)_2]_2$ (Table II) and observed and calculated structure factors from the final cycle of least-squares refinement (22 pages). Ordering information is given on any current masthead page.

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Contribution from 3M Central Research Laboratories, St. Paul, Minnesota 55101, and the Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

# 1:1 Lewis Base Adducts of Palladium Bis(hexafluoroacetylacetonate) and the Structure of $Pd(F_6acac\text{-}\mathit{C})(F_6acac\text{-}\mathit{O,O})\cdot(CH_3)_2NH$

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*Received October 16, 1980*

A series of 1:1 Lewis base adducts of palladium bis(hexafluoroacetylacetonate) of the type $Pd(F_6acac)_2\cdot L$ were prepared where L = 2,6-dimethylpyridine (**1**), 2,4,6-trimethylpyridine (**2**), phenoxathiin (**3**), phenazine (**4**), and dimethylamine (**5**). These compounds contain four-coordinate palladium with one carbon-bonded hexafluoroacetylacetonate ($F_6acac$-*C*) and one bidentate oxygen-bonded ($F_6acac$-*O,O*) ligand. This bonding pattern can be recognized by the 1:1:2 pattern of singlets in the $^{19}F$ NMR and by a strong infrared band at 1750–1730 cm$^{-1}$ due to the $(CF_3CO)_2CH$ fragment. The structure of $Pd(F_6acac)_2\cdot(CH_3)_2NH$ (**5**) was determined by single-crystal X-ray diffraction. Crystal data: space group *Pbca* (No. 61), $a = 15.448$ (5) Å, $b = 15.567$ (5) Å, $c = 16.178$ (3) Å, $V = 3891$ Å$^3$, $Z = 8$. The palladium coordination is square planar and the nearly symmetrical oxygen-bonded $F_6acac$-*O,O* ligand has a *d*(Pd–O) trans to nitrogen of 2.002 (4) Å and *d*(Pd–O) trans to carbon of 2.059 (5) Å. The palladium–nitrogen separation is 2.028 Å. The $(CF_3CO)_2CH$ moiety is approximately planar, and the dihedral angle between its plane and the palladium coordination plane is 88.4°. The Pd–$F_6acac$-*C* distance is 2.101 (7) Å.

We have previously reported that palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, has a novel and extensive acid–base chemistry. The fluorinated metalloorganic compound forms four classes of adducts with Lewis bases, L, of the type $Pd(F_6acac)_2\cdot nL$, where $n = 1$–4.[1] As part of a systematic investigation of these materials, the 1:1 adducts of $Pd(F_6acac)_2$ have been studied in detail. This paper reports their synthesis and properties and the structure of an exemplary member of the $n = 1$ class, $Pd(F_6acac)_2\cdot(CH_3)_2NH$.

## Synthesis and Properties

1:1 adducts of $Pd(F_6acac)_2$ may be prepared by direct reaction with a Lewis base in nonpolar organic solvents (cf. Experimental Section). The stability of $Pd(F_6acac)_2\cdot L_n$ with $n = 1$ relative to the $n = 2$ or 4 class appears to be determined in large part by the steric properties of the base. Thus, while pyridine reacted with $Pd(F_6acac)_2$ to yield 4:1 $Pd(F_6acac)_2\cdot 4C_5H_4N$, the more hindered 2,6-dimethylpyridine formed only $Pd(F_6acac)_2\cdot 2,6\text{-}Me_2C_5H_3N$ (**1**). With other ligands which are sterically less demanding, such as dimethylamine, 1:1, 2:1, or 4:1 adducts were obtained by adjusting the reaction conditions.

The spectroscopic properties of **1** have been studied in detail since this was one of the first $Pd(F_6acac)_2$ complexes in which the structure could be reasonably inferred from NMR and infrared data and because complexes of this type have been identified as intermediates in ortho-metalation reactions of $Pd(F_6acac)_2$.[1] **1** and the other compounds reported of the $Pd(F_6acac)_2\cdot L_n$ ($n = 1$) class have one carbon-bonded $F_6acac$ ligand ($F_6acac$-*C*) and one bidentate $F_6acac$ group bonded through the oxygen atoms ($F_6acac$-*O,O*). The $F_6acac$-*C* or, alternatively, bis(trifluoroacetyl)methyl function contains two uncoordinated $CF_3CO$ groups which are distinguished by a strong infrared absorption at 1750 cm$^{-1}$ and by a singlet of relative area 6 at 77.50 ppm in the $^{19}F$ NMR spectrum. In the $^{13}C$ spectrum, the methine carbon doublet is at rather high field ($\delta$ 29.5) with $J_{C-H} = 144$ Hz, which is reasonable for a sp$^3$ carbon bonded to two electronegative groups. Double irradiation experiments showed that the proton with $\delta$ 4.99 is coupled to this carbon atom, and it is assigned to the $(CF_3CO)_2CH$ group.

The C═O vibrations in the bidentate $F_6acac$-*O,O* function are, by analogy with other metal acetylacetonates,[2] probably not pure modes, and so the 1705- and 1640-cm$^{-1}$ bands provide, at the present level of experience, little definitive structural information. The two $CF_3$ groups in this ligand are chemically nonequivalent since one bears a transoid relationship to carbon in $F_6acac$-*C* and the other is opposite the pyridine nitrogen, and so two closely spaced singlets at 75.07 and 75.12 ppm in the $^{19}F$ NMR spectrum are seen. Thus, a 1:1:2 pattern of singlets appears to be characteristic of most carbon-bonded $Pd(F_6acac)_2\cdot L$ compounds. The $F_6acac$-*O,O* methine carbon has $\delta$ 92.2 and $J_{C-H} = 169$ Hz. The methine proton at $\delta$ 6.30 is considerably less shielded than its counterpart in the $F_6acac$-*C* moiety.

The methyl groups at the 2,6 positions in the pyridine ring are also deshielded. The $^1H$ and $^{13}C$ shifts are 3.26 and 26.7 ppm ($J_{C-H} = 128$ Hz), respectively, compared with 2.52 and 19.0 ppm in the free base. This effect is due to the magnetic anisotropy associated with the tetragonal d$^8$ system which occurs when the pyridine ring is twisted so that it is nearly perpendicular to the $PdO_2CN$ plane, a geometry observed in $(2,4,6\text{-}Me_3py)PtCl_2(C_2H_4)$.[3] The absence of large pertur-

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[1] A. R. Siedle and L. H. Pignolet, submitted for publication.

[2] K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, **83**, 1006, 1272 (1961).

**Table I.** Analytical Data

| compd | %C |  | %H |  | %N |  | mol wt |  |
|---|---|---|---|---|---|---|---|---|
|  | calcd | found | calcd | found | calcd | found | calcd | found[b] |
| $Pd(F_6acac)_2 \cdot 2,6\text{-}(CH_3)_2C_5H_3N$ (**1**) | 32.5 | 32.4 | 1.8 | 1.7 | 2.2 | 2.2 | 627 | 630 |
| $Pd(F_6acac)_2 \cdot 2,4,6\text{-}(CH_3)_3C_5H_2N$ (**2**) | 33.7 | 33.9 | 2.0 | 2.2 | 2.0 | 1.9 |  |  |
| $Pd(F_6acac)_2$·phenoxathiin (**3**) | 33.4 | 35.0 | 1.1 | 1.4 | 4.3[a] | 4.4 | 720 | 380 |
| $Pd(F_6acac)_2$·phenazine (**4**) | 37.7 | 37.8 | 1.4 | 1.3 | 4.0 | 4.1 | 700 | 520 |
| $Pd(F_6acac)_2 \cdot (CH_3)_2NH$ (**5**) | 25.5 | 25.4 | 1.6 | 1.6 | 2.5 | 2.6 |  |  |

[a] Sulfur analysis. [b] By vapor pressure osmometry in $CHCl_3$.

**Table II.** Infrared Spectra Data

| compd | $\nu_{max}$, ±5 $cm^{-1}$ (Nujol mull) |
|---|---|
| **1** | 1750 (s), 1705 (m), 1640 (m), 1615 (s), 1565 (m), 1540 (m), 1450 (s), 1270 (s), 1225 (s), 1175 (s), 1165 (s), 1155 (s), 1145 (s), 1080 (m), 1020 (s), 815 (m), 790 (s), 735 (m), 690 (m), 650 (m) |
| **2** | 1745 (s), 1700 (m), 1630 (s), 1610 (m), 1560 (m), 1530 (w), 1450 (s), 1255 (s), 1220 (m), 1200 (s), 1150 (s), 1110 (m), 1080 (m), 1025 (m), 850 (m), 800 (m), 790 (m), 730 (m), 685 (s), 645 (m) |
| **3** | 3150 (w), 1735 (s), 1690 (w), 1630 (s), 1610 (s), 1600 (s), 1595 (m), 1560 (m), 1470 (s), 1455 (m), 1445 (s), 1320 (m), 1260 (s), 1205 (s), 1160 (s), 1100 (s), 1085 (s), 1030 (m), 860 (s), 855 (s), 755 (s), 685 (m), 650 (m) |
| **4** | 3150 (w), 1750 (s), 1700 (m), 1630 (s), 1610 (s), 1560 (m), 1520 (m), 1455 (s), 1435 (m), 1270 (s), 1225 (s), 1210 (s), 1160 (sh), 1145 (s), 1120 (w), 1110 (s), 1080 (s), 1030 (s), 835 (m), 810 (m), 750 (s), 690 (m), 650 (m), 590 (m), 570 (w) |
| **5**[a] | 3220 (w), 1725 (s), 1680 (w), 1630 (s), 1610 (w), 1560 (m), 1530 (m), 1455 (s), 1430 (m), 1260 (s), 1205 (s), 1155 (s), 1110 (w), 1090 (m), 1030 (m), 800 (m), 785 (m), 690 (m), 655 (m) |

[a] KBr disk.

**Table III.** NMR Spectral Data

| compd | δ (splitting,[a] assignt) |
|---|---|
| **1** | $^{19}F$: 75.07 (1 F), 75.12 (1 F), 77.50 (2 F)<br>$^{13}C$: 160.6 [s, C(2) in $(CH_3)_2C_5H_3N$], 140.2 [d, 167, C(4)], 124.5 [d, 169, C(3)], 92.2 (d, 169, $F_6$acac-*O,O* CH), 29.5 (d, 144, $F_6$acac-*C* CH), 26.7 (q, 128, $CH_3$)<br>$^1H$: 7.77 (t, 8, $C_4H$), 7.26 (d, 8, $C_{3,5}H$), 6.30 (s, $F_6$acac-*O,O* CH), 4.99 (s, $F_6$acac-*C* CH), 3.26 (s, $CH_3$) |
| **2** | $^{19}F$: 75.10 (1 F), 75.15 (1 F), 77.44 (2 F)<br>$^1H$: 7.03 (s, $C_{3,5}H$), 6.30 (s, $F_6$acac-*O,O* CH), 4.99 (s, $F_6$acac-*C* CH), 3.18 (s, 2,6-$CH_3$), 2.41 (s, 4-$CH_3$) |
| **3** | $^{19}F$: 75.20 (1 F), 75.28 (1 F), 77.02 (2 F)<br>$^1H$: 6.12 ($F_6$acac-*O,O* CH), 5.36 ($F_6$acac-*C* CH) |
| **4** | $^{19}F$: 74.82 (1 F), 74.88 (1 F), 77.36 (2 F)<br>$^1H$: 9.8 (d, $C_{12}H_8N_2$ peri H), 6.47 ($F_6$acac-*O,O* CH), 5.02 ($F_6$acac-*C* CH) |
| **5** | $^{19}F$: 74.11 (1 F), 75.38 (1 F), 77.35 (2 F)<br>$^1H$: 6.28 (s, $F_6$acac-*O,O* CH), 5.31 (s, $F_6$acac-*C* CH), 3.47 (NH), 2.37 (d, $^3J_{HCNH}$ = 5.6, $CH_3$) |

[a] *J* values in Hz.

bations in the pyridine ring current is indicated by the proton spectrum of $Pd(F_6acac\text{-}C)(F_6acac\text{-}O,O) \cdot 2,4,6\text{-}(CH_3)_3C_5H_2N$ (**2**) in which the 4-methyl group has δ 2.41, the same as in the free ligand, whereas the methyl groups are significantly shielded with δ 3.18, compared with 2.37 in pure 2,4,6-$(CH_3)_3C_5H_2N$.

Phenazine and phenoxathiin are also bulky ligands on account of the space occupied by the peri hydrogens. These heterocycles formed the 1:1 adducts $Pd(F_6acac\text{-}C)(F_6acac\text{-}O,O) \cdot L$ (for **3** L = phenoxathiin, for **4** L = phenazine) as indicated by elemental analyses (Table I), characteristic carbonyl bands at 1735–1750 $cm^{-1}$ in the infrared spectra (Table II), and $^1H$ and $^{19}F$ NMR data (Table III). (See eq 1.) These donors, however, are weakly bound, and the adducts

$$Pd(F_6acac)_2 + L \rightleftarrows Pd(F_6acac\text{-}C)(F_6acac\text{-}O,O) \cdot L \quad (1)$$

are largely dissociated in solution. The formation constants for **3** and **4** obtained by integration of the $^{19}F$ NMR spectra were 5 × $10^{-3}$ and 8.3 × $10^{-3}$, respectively, in $CDCl_3$ at 27 °C. The $^1H$ NMR spectrum of **4** shows a resonance at 9.8 ppm characteristic of phenazine peri protons which, from molecular models, lie close to and are deshielded by the transition metal.[4]

The reaction of $Pd(F_6acac)_2$ in pentane with a limited amount of dimethylamine produced both $Pd(F_6acac)_2 \cdot 2(CH_3)_2NH$ and $Pd(F_6acac\text{-}C)(F_6acac\text{-}O,O) \cdot (CH_3)_2NH$ (**5**). The $^{19}F$ NMR spectrum of **5** showed three singlets at 75.11, 75.38, and 77.35 ppm in a 1:1:2 ratio. The $^1H$ NMR spectrum in $CDCl_3$ revealed δ($F_6$acac-*C*) 5.31 and δ($F_6$acac-*O,O*) 6.28. The methyl protons have δ 2.37 and a field independent 5.6-Hz coupling to the N–H proton at δ 3.47. An X-ray crystallographic analysis of **5** was carried out in order to further characterize this class of $Pd(F_6acac)_2$ adducts.

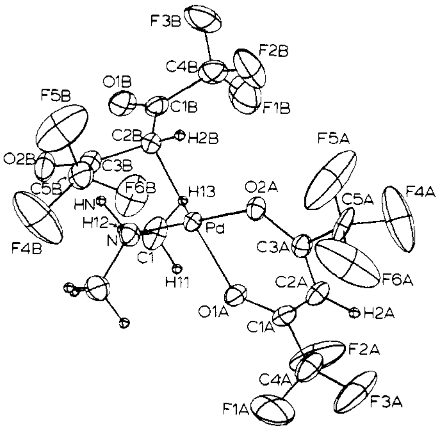

**Figure 1.** ORTEP drawing of $Pd(F_6acac\text{-}C)(F_6acac\text{-}O,O) \cdot (CH_3)_2NH$ showing the labeling scheme.

## Description of the Structure

The crystal structure of $Pd(F_6acac\text{-}C)(F_6acac\text{-}O,O) \cdot (CH_3)_2NH$ consists of discrete molecular units. The shortest intermolecular contacts are between fluorine atoms (F3A⋯F4B = 2.94 (1) Å). There are two distinct coordination modes for the $F_6$acac ligands. The A ligand is chelated in a normal bidentate fashion via the two oxygen atoms whereas the B ligand bonds in a monodentate fashion via the central carbon atom. The molecular geometry is shown in Figures 1–3, and selected distances and angles are presented in Table IV.

The coordination geometry about the palladium atom in $Pd(F_6acac\text{-}C)(F_6acac\text{-}O,O) \cdot (CH_3)_2NH$ is approximately

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[3] F. Caruso, R. Spagua, and L. Zambonelli, *J. Cryst. Mol. Struct.*, **8**, 47 (1979).

[4] A. R. Siedle and F. J. Palensky, unpublished results.

**Table IV.** Selected Distances and Angles[a]

| | | | | | |
|---|---|---|---|---|---|
| | | Distances, Å | | | |
| Pd–O1A | 2.059 (5) | O1A–C1A | 1.278 (8) | C2A–C1A | 1.40 (1) |
| Pd–O2A | 2.002 (4) | O2A–C3A | 1.284 (7) | C2A–C3A | 1.34 (1) |
| Pd–C2B | 2.101 (7) | O1B–C1B | 1.188 (9) | C1A–C4A | 1.49 (1) |
| Pd–N | 2.028 (6) | O2B–C3B | 1.234 (9) | C3A–C5A | 1.46 (1) |
| N–C1 | 1.49 (1) | C2B–C1B | 1.48 (1) | C1B–C4B | 1.50 (1) |
| N–C2 | 1.44 (1) | C2B–C3B | 1.46 (1) | C3B–C5B | 1.49 (1) |
| C4A–F1A | 1.27 (1) | C4A–F2A | 1.22 (1) | C4A–F3A | 1.24 (1) |
| C5A–F4A | 1.19 (1) | C5A–F5A | 1.16 (1) | C5A–F6A | 1.20 (1) |
| C4B–F1B | 1.35 (1) | C4B–F2B | 1.28 (1) | C4B–F3B | 1.30 (1) |
| C5B–F4B | 1.29 (1) | C5B–F5B | 1.26 (1) | C5B–F6B | 1.31 (1) |
| | | Angles, Deg | | | |
| O1A–Pd–O2A | 92.5 (2) | Pd–O1A–C1A | 121.7 (5) | C1A–C2A–C3A | 126.5 (6) |
| O1A–Pd–N | 88.5 (2) | Pd–O2A–C3A | 123.4 (5) | O1A–C1A–C2A | 127.5 (6) |
| O1A–Pd–C2B | 177.8 (2) | Pd–C2B–C1B | 101.8 (5) | O1A–C1A–C4A | 113.1 (7) |
| O2A–Pd–N | 178.1 (2) | Pd–C2B–C3B | 103.7 (5) | O2A–C3A–C2A | 128.0 (7) |
| O2A–Pd–C2B | 86.3 (2) | Pd–N–C1 | 112.2 (5) | O2A–C3A–C5A | 110.9 (7) |
| N–Pd–C2B | 92.7 (3) | Pd–N–C2 | 111.7 (5) | C1–N–C2 | 110.0 (7) |
| C2B–C1B–O1B | 126.5 (7) | C2B–C3B–O2B | 125.7 (7) | O1B–C1B–C4B | 117.4 (8) |
| C2B–C1B–C4B | 116.0 (7) | C2B–C3B–C5B | 118.4 (7) | O2B–C3B–C5B | 115.8 (7) |
| C2A–C1A–C4A | 119.3 (7) | C2A–C3A–C5A | 120.7 (7) | C1B–C2B–C3B | 119.4 (6) |

[a] The numbers in parentheses are the esd's of the last significant figure.

**Table V**

Least-Squares Planes[a]

| plane no. | *A* | *B* | *C* | *D* | atom | *X* | *Y* | *Z* | dist, Å |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.8376 | −0.4119 | −0.3588 | −0.8601 | O1A$^b$ | 1.8908 | 1.9001 | 4.5905 | 0.014 |
| | | | | | O2A$^b$ | 0.9683 | −0.7172 | 5.5454 | −0.023 |
| | | | | | C1A$^b$ | 2.3655 | 1.8856 | 5.7773 | −0.008 |
| | | | | | C2A$^b$ | 2.2560 | 0.8649 | 6.7240 | −0.019 |
| | | | | | C3A$^b$ | 1.6647 | −0.3217 | 6.5493 | 0.037 |
| | | | | | PD$^c$ | 0.8200 | 0.3122 | 3.8344 | 0.043 |
| | | | | | C4A$^c$ | 3.0605 | 3.1554 | 6.1470 | −0.082 |
| | | | | | C5A$^c$ | 1.6195 | −1.2987 | 7.6321 | 0.013 |
| | | | | | H2A$^c$ | 2.6237 | 1.0231 | 7.5412 | −0.070 |
| 2 | 0.8410 | −0.4375 | −0.3184 | −0.6703 | O1A$^b$ | 1.8908 | 1.9001 | 4.5905 | −0.032 |
| | | | | | O2A$^b$ | 0.9683 | −0.7172 | 5.5454 | 0.033 |
| | | | | | N$^b$ | 0.7021 | 1.3033 | 2.0692 | 0.032 |
| | | | | | C2B$^b$ | −0.3281 | −1.2971 | 3.1225 | −0.032 |
| | | | | | Pd$^c$ | 0.8200 | 0.3122 | 3.8344 | 0.003 |
| 3 | −0.5232 | −0.8403 | −0.1423 | 0.9165 | O1B$^b$ | −1.9873 | −0.1358 | 1.8624 | −0.028 |
| | | | | | O2B$^b$ | 0.3608 | −1.4169 | 0.8251 | −0.032 |
| | | | | | C1B$^b$ | −1.6345 | −0.6507 | 2.8734 | 0.077 |
| | | | | | C2B$^b$ | −0.3281 | −1.2971 | 3.1225 | −0.099 |
| | | | | | C3B$^b$ | 0.4490 | −1.8053 | 1.9929 | 0.082 |
| | | | | | C4B$^c$ | −2.5703 | −0.5906 | 4.0408 | 0.350 |
| | | | | | C5B$^c$ | 1.3466 | −2.9529 | 2.2904 | 0.534 |
| | | | | | H2B$^c$ | −0.3412 | −1.6482 | 3.8738 | 0.096 |

Dihedral Angles between Planes

| plane no. | plane no. | dihedral angle, deg |
|---|---|---|
| 1 | 2 | 2.7 |
| 1 | 3 | −87.6 |
| 2 | 3 | −88.4 |

[a] The equation of the plane is of the form $A^*X + B^*Y + C^*Z - D = 0$, where *A*, *B*, *C*, and *D* are constants and *X*, *Y*, and *Z* are orthogonalized. [b] Atoms in the plane. [c] Other atoms.

square planar as shown in Figures 2 and 3 and Table V. The Pd atom is displaced only 0.003 Å from the least-squares plane formed by O1A, O2A, N, and C2B (plane 1, Table V). The bidentate, oxygen-bonded $F_6$acac-*O,O* ligand is planar within experimental error (plane 2, Table V), and the dihedral angle between planes 1 and 2 is 2.7°.

The $F_6$acac-*O,O* ligand is unsymmetrically bonded to palladium, and the Pd–O1A and Pd–O2A distances are 2.059 (5) and 2.002 (4) Å, respectively. These distances are similar to a *d*(Pd–O) of 2.08 Å in cycloocta-2,4-dienylpalladium acetylacetonate[5] and 2.050 and 2.077 Å in ($\pi$-pentamethylbicyclo[2.2.0]hexa-2,5-dienylmethyl)palladium acetylacetonate,[6] but the difference between them 0.057 Å, is much greater than that, 0.01 Å, in Pd(acac-*C*)(acac-*O,O*)$PPh_3 \cdot 0.5C_6H_6$.[7] In that compound, *d*(Pd–O) trans to the carbon-bonded acetylacetonate ligand was 2.06 (1) Å and *d*(Pd–O) trans to triphenylphosphine was 2.05 (1) Å. The large differences between the Pd–O separations in **5** can be attributed to the different structural trans effect of dimethylamine and the $(CF_3CO)_2CH$ group, that of the latter being greater.

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(7) M. Horike, Y. Kai, N. Yasuoka, and N. Kasai, *J. Organomet. Chem.*, **72**, 441 (1974).

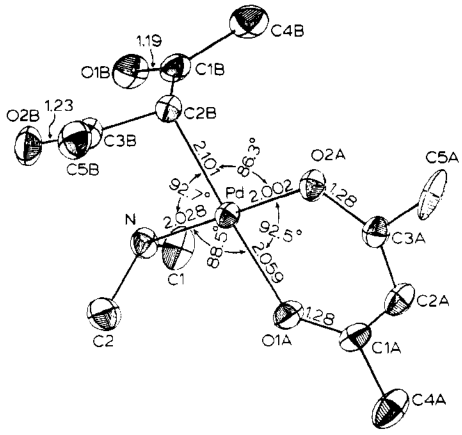

**Figure 2.** ORTEP drawing of the coordination core in Pd($F_6$acac-*C*)($F_6$acac-*O*,*O*)·$(CH_3)_2NH$.

The two C–O distances in the $C_3O_2Pd$ chelate ring, *d*(C3A–O2A) = 1.284 (7) Å, and *d*(C1A–O1A) = 1.278 Å, are the same within experimental error and much longer than the 1.231 Å distance found in the weakly coordinated $F_6$acac groups found in Pd($F_6$acac)$_2$(4-$ClC_5H_4$)$_4$.[8] Further traces of asymmetry in the $F_6$acac-*O*,*O* ligand are found in the C–C and C–F distances in the $C_3(CF_3)_2$ portion of this group, where differences in bond lengths are greater than 3$\sigma$. Thus, the C1A–C2A and C2A–C3A bond distances are 1.40 (1) and 1.34 (1) Å, respectively. Similarly, *d*(C1A–C4A) (1.49 (1) Å) is slightly longer than *d*(C3A–C5A) (1.46 Å), and *d*(C5A–F)$_{av}$ (1.18 (1) Å) is slightly shorter than *d*(C4A–F)$_{av}$ (1.24 (1) Å). Thus, the trans influence is attenuated with increasing distance from the metal and bond alternations involving fluorine and C1A, C2A, C3A, C4A, and C5A are small. This is in contrast to the significant alternation of short and long bond lengths found by Pradilla-Sorzano and Fackler[9] in the chelate rings in Cu($F_6$acac)$_2$·2$C_5H_5N$ and Zn-($F_6$acac$_2$)$_2$·2$C_5H_5N_5$.

The carbon-bonded $F_6$acac group is connected to the metal with a Pd–C2B distance of 2.101 (7) Å, a bond length which is in good agreement with the Pd–C distances of 2.114 Å in Pd(acac-*C*)(acac-*O*,*O*)$PPh_3$·0.5$C_6H_6$ and 1.99 Å in *trans*-chloro-2-(phenylazo)phenylbis(triethylphosphine)palladium.[10] This $F_6$acac-*C* moiety is approximately planar (plane 3, Table V) but oriented so that the least-squares plane formed by O1B, O2B, C1B, C2B, and C3B makes a dihedral angle of 88.4° with the O1A, O2A, N, C2B coordination plane. This is clearly evident in Figure 3. The angles about C2B approach 109° as expected for a sp$^3$ carbon, but the C3B–C2B–C1B angle (119°) is considerably expanded, pushing the $COCF_3$ groups apart.[11]

The dimethylamine ligand is bonded through an approximately tetrahedral nitrogen to palladium, and C1–N–C2 is 110.0 (7)°. The Pd–N distance (2.028 (6) Å) is comparable to, for example, 1.987 Å in (en)$PdCl_2$[12] and 2.024 Å in bis(tri-*p*-tolylformazanyl)palladium.[13]

## Experimental Section

**Pd($F_6$acac)$_2$·2,6-$(CH_3)_2C_5H_3N$ (1).** Palladium bis(hexafluoroacetylacetonate) (0.2 g) in 8 mL of pentane was treated with excess 2,6-dimethylpyridine. The orange solution was briefly cooled in a dry ice bath and then filtered to afford 0.19 g of the solid product. This was recrystallized from hexane to provide fibrous yellow needles of **1**, mp 131–132 °C. Mass spectrum (70 eV, on the basis of $^{106}$Pd): 627 ($M^+$), 608 ($M^+$ – F), 558 ($M^+$ – $CF_3$), 520 (Pd($F_6$acac)$_2^+$). $\lambda_{max}$($CH_3CN$) = 303 nm (log $\epsilon$ = 4.44). Pd($F_6$acac)$_2$·2,4,6-$(CH_3)_3C_5H_2N$ (**2**), mp 145–146 °C, was prepared in a similar manner.

**Pd($F_6$acac)$_2$·phenoxathiin (3).** Palladium bis(hexafluoroacetylacetonate) (0.26 g, 0.5 mmol) and phenoxathiin (0.20 g, 1.0 mmol) were combined in 6 mL of hexane. The orange solution was cooled to –78 °C. The solids which separated were collected on a filter and then heated (warm water bath) in a vacuum sublimer fitted with a dry ice cooled probe. The nonvolatile orange crystals of the product (0.20 g) remained; mp 92–93 °C. Crystal data: space group $P2_1/c$, $a$ = 10.090 (3) Å, $b$ = 19.398 (3) Å, $c$ = 17.263 (3) Å, $\beta$ = 93.85 (2)°.

**Pd($F_6$acac)$_2$·phenazine (4).** Palladium bis(hexafluoroacetylacetonate) (0.52 g, 1 mmol) and phenazine (0.18 g, 1 mmol) and 8 mL of hot toluene were combined. On cooling of the solution in a dry-ice bath, yellow flakes separated. These were heated (50 °C, 2 × 10$^{-3}$ mmHg) in a sublimer fitted with a dry ice cooled probe. The residue weighed 0.20 g and was the 1:1 adduct, mp >300 °C.

**Pd($F_6$acac)$_2$·$(CH_3)_2NH$ (5).** Dry dimethylamine was bubbled into a solution of 0.4 g of Pd($F_6$acac)$_2$ in 10 mL of pentane until yellow crystals just began to separate. Slow evaporation of the resulting solution afforded opaque yellow crystals of Pd($F_6$acac)$_2$·2$(CH_3)_2NH$ and clear orange crystals of the 1:1 adduct **5**. The latter were mechanically removed and had mp 128–130 °C.

**Structure Determination.** A crystal of Pd($F_6$acac-*C*)$_2$·$(CH_3)_2NH$, $PdF_{12}O_4NC_{12}H_9$ (formula weight 565.6), of approximate dimensions 0.35 × 0.10 × 0.15 nm was selected and used in the structure determination. The crystal was found to belong to the orthorhombic crystal class by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing programs. The space group *Pbca* (No. 61) was chosen from the systematic absences observed during data collection ($0kl$, $k = 2n + 1$; $h0l$, $l = 2n + 1$; $hk0$, $h = 2n + 1$) and was verified by successful solution and refinement (vide infra). The unit cell dimensions were determined by least-squares refinement of the angular settings of 25 peaks centered on the diffractometer and are $a$ = 15.448 (5) Å, $b$ = 15.567 (5) Å, $c$ = 16.178 (3) Å, and $V$ = 3891 (3) Å$^3$. The density is calculated to be 1.931 g/cm$^3$ on the assumption of $Z$ = 8.

Data collection was carried out with use of a CAD4 Nonius automatic diffractometer. Background counts were measured at both ends of the scan range with use of a variable rate $\omega$–$2\theta$ scan equal, at each side, to one-fourth of the scan range of the peak. In this manner, the total duration of measuring backgrounds is equal to half of the time required for the peak scan. The intensities of three standard reflections were measured every 1.5 h of X-ray exposure, and a uniform decay in the intensities of the three reflections was observed. A decay correction was applied to the data (corrections: minimum, 1.00; maximum, 1.31; average, 1.16). The intensities of 3426 ($+h$, $+k$, $+l$) unique reflections were measured at room temperature out to $2\theta$ of 50° with use of Mo K$\alpha$ radiation ($\lambda$ = 0.71069 Å). After correction for Lorentz, polarization, and background effects (but not for absorption, $\mu$ = 10.8 cm$^{-1}$),[14] 2051 reflections were judged observed [$F_o^2 \geq 2.5\sigma(F_o^2)$] and were used in all subsequent calculations.[15]

Conventional heavy-atom techniques were used to solve the structure and refinement, with all nonhydrogen atoms thermally anisotropic by full-matrix least-squares methods (271 variables). $R$ and $R_w$ converged to their final values of 0.055 and 0.077, respectively.[16] The

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(8) A. R. Siedle, R. A. Newmark, and L. H. Pignolet, submitted for publication.

(9) J. Pradilla-Sorzano and J. P. Fackler, *Inorg. Chem.*, **12**, 1174 (1973).

(10) D. L. Weaver, *Inorg. Chem.*, **9**, 2250 (1970).

(11) The literature on metal complexes in which a monodentate acetylacetonate group is linked by the central carbon atom has been summarized by S. Komiya and J. K. Kochi, *J. Am. Chem. Soc.*, **99**, 3695 (1977).

(12) J. Iball, M. MacDougal, and S. Scrimgeour, *Acta Crystallogr., Sect. B*, **31B**, 1672 (1975).

(13) A. R. Siedle and L. H. Pignolet, *Inorg. Chem.*, **19**, 2052 (1980).

(14) Intensity data were processed as described in the "CAD4 and SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity $I$ is given by $I = (K/\mathrm{NPI})(C - 2B)$, where $K$ = 20.1166 × (attenuator factor), NPI = ratio of fastest possible scan rate to scan rate for the measurement, $C$ = total count, and $B$ = total background count. The standard deviation in the net intensity is given by $\sigma^2(I) = (K/\mathrm{NPI})^2[C + 4B + (pI)^2]$, where $p$ is a factor used to downweight intense reflections. The observed structure factor amplitude $F_o$ is given by $F_o = (I/Lp)^{1/2}$, where $Lp$ = Lorentz and polarization factors. The $\sigma(I)$'s were converted to the estimated errors in the relative structure factors $\sigma(F_o)$ by $\sigma(F_o) = {}^1/_2(\sigma(I)/I)F_o$.

(15) Calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described by B. A. Frenz in "Computing Crystallography", H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, G. C. Bassi, Eds., Delft University Press, Delft, Holland, 1978, pp 64–71.

error in an observation of unit weight was determined to be 1.99 by using a value of 0.04 for $p$ in the $\sigma(I)$ equation. Hydrogen atom positions were located by difference Fourier analysis and were included in the structure factor calculation of the final least-squares cycles but were not refined.

The final atomic coordinates with their esd's and the final thermal parameters are given in Table VI. Tables of observed and calculated structure factor amplitudes are available (supplementary material). Figure 1 presents an ORTEP perspective of the molecular structure and shows the labeling scheme.

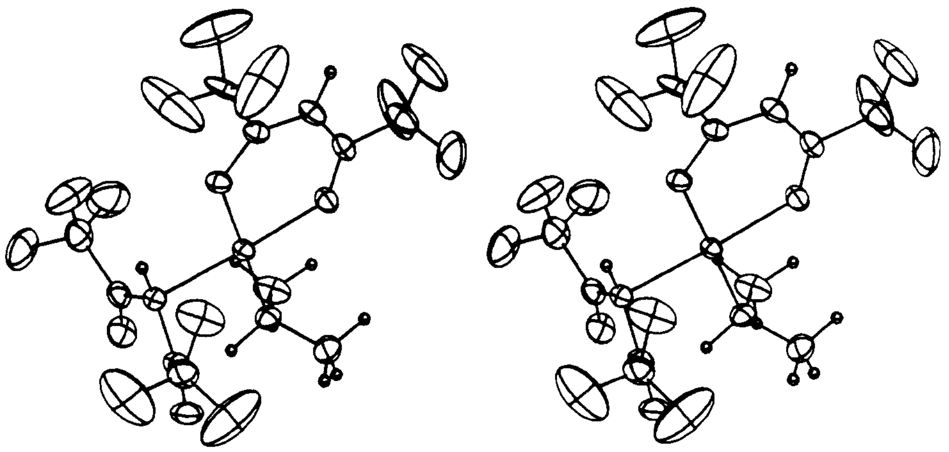

**Figure 3.** ORTEP stereoview of the molecule.

**Table VI.** Positional and Thermal Parameters and Their Estimated Standard Deviations[a]

| atom | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Pd | 0.05308 (4) | 0.02005 (5) | 0.23701 (4) | 3.89 (2) | 3.92 (3) | 3.29 (2) | −0.00 (3) | −0.46 (2) | −0.04 (3) |
| F1A | 0.2602 (6) | 0.2203 (6) | 0.3317 (8) | 15.6 (5) | 12.5 (5) | 23.2 (9) | −9.6 (4) | 7.7 (6) | −6.6 (6) |
| F2A | 0.1537 (6) | 0.2669 (5) | 0.3742 (8) | 11.3 (5) | 5.4 (4) | 34 (1) | 0.4 (4) | −8.2 (6) | −6.3 (5) |
| F3A | 0.2337 (7) | 0.2031 (6) | 0.4486 (6) | 28.6 (7) | 12.0 (5) | 13.7 (5) | −111 (4) | −12. (4) | 2.8 (4) |
| F1B | −0.1745 (7) | 0.0439 (7) | 0.2766 (6) | 15.2 (7) | 12.3 (6) | 13.2 (6) | 1.5 (6) | 4.2 (5) | −2.9 (5) |
| F2B | −0.1471 (5) | −0.0812 (7) | 0.3146 (4) | 8.2 (4) | 21.7 (8) | 7.6 (4) | 4.1 (5) | 2.0 (3) | 5.2 (4) |
| F3B | −0.2449 (5) | −0.0594 (7) | 0.2290 (5) | 4.7 (3) | 17.4 (8) | 12.9 (5) | −0.8 (4) | 0.9 (4) | 2.9 (5) |
| F4B | 0.1547 (6) | −0.1911 (8) | 0.0949 (7) | 13.4 (5) | 24.0 (8) | 19.0 (7) | 11.2 (5) | 8.7 (5) | 9.8 (6) |
| F5B | 0.0528 (7) | −0.2620 (6) | 0.1308 (8) | 18.6 (7) | 7.0 (4) | 25 (1) | 4.4 (5) | −8.3 (7) | −5.3 (5) |
| F6B | 0.1196 (5) | −0.1927 (5) | 0.2160 (5) | 12.0 (5) | 9.8 (4) | 9.6 (4) | 5.0 (4) | −3.2 (4) | −1.7 (4) |
| F4A | 0.0826 (8) | −0.0611 (6) | 0.5387 (5) | 33 (1) | 14.2 (6) | 9.0 (4) | 11.1 (6) | 5.3 (5) | 6.0 (4) |
| F5A | 0.0678 (9) | −0.1477 (6) | 0.4634 (5) | 55 (1) | 13.2 (5) | 13.4 (4) | −18 (6) | −191 (5) | 9.0 (4) |
| F6A | 0.1751 (6) | −0.1107 (7) | 0.4901 (6) | 11.4 (5) | 26.1 (6) | 27.8 (6) | 6.5 (5) | 4.5 (5) | 22.3 (4) |
| O1A | 0.1224 (4) | 0.1221 (4) | 0.2837 (4) | 5.5 (3) | 4.5 (3) | 5.0 (3) | −1.0 (3) | −1.0 (2) | −0.1 (2) |
| O2A | 0.0627 (4) | −0.0461 (4) | 0.3428 (3) | 5.5 (3) | 4.1 (3) | 3.3 (2) | 0.1 (2) | −0.4 (2) | 0.1 (2) |
| O1B | −0.1286 (4) | −0.0087 (5) | 0.1151 (4) | 5.5 (3) | 8.5 (4) | 6.5 (4) | 0.3 (3) | −2.2 (3) | 1.3 (3) |
| O2B | 0.0234 (5) | −0.0910 (5) | 0.0510 (4) | 9.2 (4) | 7.5 (4) | 3.6 (3) | −0.3 (4) | 0.1 (3) | −0.8 (3) |
| N | 0.0454 (5) | 0.0837 (5) | 0.1279 (4) | 6.4 (4) | 4.9 (4) | 3.7 (3) | −0.3 (3) | −0.1 (3) | 0.8 (3) |
| C1A | 0.1531 (5) | 0.1211 (6) | 0.3571 (6) | 3.7 (4) | 4.4 (4) | 5.8 (4) | 0.2 (4) | −1.1 (4) | −1.0 (4) |
| C2A | 0.1460 (6) | 0.0556 (6) | 0.4156 (5) | 5.6 (4) | 5.3 (5) | 4.4 (4) | −0.0 (4) | −2.1 (4) | −0.2 (4) |
| C3A | 0.1078 (5) | −0.0207 (6) | 0.4048 (5) | 4.5 (4) | 4.7 (4) | 3.6 (3) | 0.4 (4) | −0.6 (3) | −0.0 (4) |
| C4A | 0.1981 (8) | 0.2027 (7) | 0.3800 (7) | 10.9 (8) | 4.6 (5) | 6.9 (6) | −1.8 (5) | −3.1 (5) | 0.2 (5) |
| C5A | 0.1048 (8) | −0.0834 (7) | 0.4718 (5) | 10.8 (7) | 5.8 (5) | 3.8 (4) | 2.7 (5) | −4.6 (4) | −1.6 (4) |
| C1B | −0.1058 (6) | −0.0418 (7) | 0.1776 (6) | 4.2 (4) | 6.0 (5) | 5.2 (4) | −0.4 (4) | −1.3 (4) | −0.1 (4) |
| C2B | −0.0212 (5) | −0.0833 (6) | 0.1930 (5) | 4.1 (4) | 4.4 (4) | 3.8 (4) | −0.1 (3) | −0.1 (3) | −0.2 (3) |
| C3B | 0.0291 (6) | −0.1160 (7) | 0.1232 (6) | 6.5 (5) | 4.6 (5) | 4.4 (4) | −0.5 (4) | −0.5 (4) | −0.4 (4) |
| C4B | −0.1664 (8) | −0.0379 (9) | 0.2498 (7) | 4.2 (4) | 8.2 (7) | 9.2 (7) | 0.5 (5) | −0.5 (5) | −1.1 (6) |
| C5B | 0.0872 (7) | −0.1897 (7) | 0.1416 (7) | 6.0 (5) | 6.3 (6) | 7.2 (6) | 1.0 (5) | 0.6 (5) | −2.3 (5) |
| C1 | 0.0012 (8) | 0.1690 (8) | 0.1366 (7) | 10.5 (7) | 5.4 (5) | 5.9 (5) | 2.8 (5) | −2.7 (5) | 0.4 (4) |
| C2 | 0.1292 (7) | 0.0949 (8) | 0.0910 (6) | 7.2 (6) | 7.7 (6) | 5.2 (5) | −1.3 (5) | 0.0 (5) | 1.4 (5) |

| atom | $x$ | $y$ | $z$ | $B$, Å$^2$ | atom | $x$ | $y$ | $z$ | $B$, Å$^2$ |
|---|---|---|---|---|---|---|---|---|---|
| H2B | −0.0221 (0) | −0.1059 (0) | 0.2395 (0) | 5.0000 (0) | H22 | 0.1728 (0) | 0.1208 (0) | 0.1299 (0) | 8.0000 (0) |
| H12 | −0.0143 (0) | 0.1901 (0) | 0.0788 (0) | 8.0000 (0) | HN | 0.0075 (0) | 0.0472 (0) | 0.0899 (0) | 8.0000 (0) |
| H11 | 0.0416 (0) | 0.2108 (0) | 0.1653 (0) | 8.0000 (0) | H23 | 0.1175 (0) | 0.1358 (0) | 0.0430 (0) | 8.0000 (0) |
| H13 | −0.0527 (0) | 0.1638 (0) | 0.1723 (0) | 8.0000 (0) | H2A | 0.1698 (0) | 0.0657 (0) | 0.4661 (0) | 5.0000 (0) |
| H21 | 0.1554 (0) | 0.0384 (0) | 0.0697 (0) | 8.0000 (0) | | | | | |

[a] The form of the anisotropic thermal parameter is $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

**Registry No. 1**, 76946-88-8; **2**, 76946-87-7; **3**, 76946-86-6; **4**, 76946-85-5; **5**, 76946-84-4; $Pd(F_6acac)_2$, 64916-48-9.

**Supplementary Material Available:** A listing of structure factor amplitudes (9 pages). Ordering information is given on any current masthead page.

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(16) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are defined as $R = (\sum||F_o| - |F_c||)/\sum|F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|))^2/(\sum w|F_o|)^2]^{1/2}$. The error in an observation of unit weight is $[\sum w(|F_o| - |F_c|)^2/(NO - NV)]^{1/2}$ where NO and NV are the number of observations and variables, respectively. Atomic scattering factors were taken from the "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962. Anomalous dispersion corrections from the same source were used for palladium.