

(EDTA)²⁻ and H(NTA)²⁻ and also between VO₂EDDA⁻ and H(NTA)²⁻ and between VO₂EDDA⁻ and H₂NTA⁻.

There exist several paths of reaction via the formation of outer-sphere complexes between the reacting chelates and the entering aminocarboxylate ligands. These reactions are followed by ligand interchanges, which are the limiting steps of the reactions. For example, we propose, in Figure 3, a scheme for the ligand-exchange reaction between VO₂EDTA³⁻ and H(NTA)²⁻. The first step is a fast formation of an outer-sphere preequilibrium complex. The structure of the VO₂EDTA³⁻ complex, with no water bonded to the vanadium and no very weak vanadium-ligand bond, and the lack of significant variation of the spectrum between 220 and 400 nm during this first step lead us to postulate the formation of this outer-sphere complex. The following steps might be reactions of interchange between one chelating group of EDTA bonded to the metal and one entering chelating group of NTA. The

cleavage of a metal-EDTA nitrogen bond must be the key process. All these interchange reactions between chelating groups of the leaving ligand and chelating groups of the entering ligand are apparently first order as the reactions occur in outer-sphere complexes and do not involve direct attack of external species. Thus the rate constants of the ligand-interchange reactions must be of the same order of magnitude (0.1-0.6 s⁻¹) as we have experimentally shown. This is due to the fact that in all reactions, the broken and new bonds are almost the same.

In conclusion, the results presented above show that the mechanism of chelating group exchange reactions depends on whether the central metal is or is not bonded to water molecules.

Registry No. VO₂EDTA³⁻, 68907-94-8; VO₂EDDA⁻, 38868-05-2; H₂NTA, 139-13-9.

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4:1 Lewis Base Adducts of Palladium Bis(hexafluoroacetylacetonate). The Structure of (4-ClC₃H₄N)₄Pd(C₅HF₆O₂)₂

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Palladium bis(hexafluoroacetylacetonate), Pd(F₆acac)₂, reacts with a wide variety of Lewis bases to form 4:1 adducts of the type (L₄Pd₂)(F₆acac)₂ where L includes (CH₃)₂NH, CH₃NH₂, NH₃, C₅H₅N, imidazole, 3,5-(CH₃)₂pyrazole, *t*-C₄H₉NC, Ph₃Sb, benzothiazole, and 1,3-dithiolene-2-thione and the chelating bidentate ligands Ph₂PC₂H₄PPh₂, Ph₂PCH₂PPh₂, Ph₂AsC₂H₄AsPh₂, and 1,4-C₄H₈S₂. Metathesis with NH₄PF₆ yields (L₄Pd)(PF₆)₂. These compounds were characterized by conductivity and spectroscopic measurements. The 4-chloropyridine adduct (4-ClC₃H₄N)₄Pd(F₆acac)₂ was characterized by single-crystal X-ray diffraction. Crystal data: space group P2₁/c, *a* = 19.356 (3) Å, *b* = 18.902 (3) Å, *c* = 10.636 (2) Å, β = 100.12°, *V* = 3831 Å³. There are two crystallographically independent molecules per unit cell. Both F₆acac groups have been displaced, and the pyridine rings in the (4-ClC₃H₄N)₄Pd group are mutually perpendicular and *d*(Pd-N)_{av} in the planar PdN₄ unit is 2.029 Å. Two oxygens, one from each F₆acac, occupy axial positions with *d*(Pd-O) = 3.02 Å.

Introduction

The chemistry of palladium bis(hexafluoroacetylacetonate), Pd(F₆acac)₂, is extensive in scope. It is a strong Lewis acid and with molecular bases forms adducts of the general formula Pd(F₆acac)₂(ligand)_{*n*} where *n* = 1, 2, 3, or 4. Previous papers from these laboratories have characterized the *n* = 1 and 2 classes of adducts² and their role in ortho metalation³ and β-diketonate transfer reactions⁴ as well as acid-base surface complexes formed with use of metal oxides as condensed-phase donors.^{5,6} This paper describes the synthesis and properties of the *n* = 4 class, Pd(F₆acac)₂(ligand)₄, and reports the crystal structure of a representative member, Pd(F₆acac)₂(4-ClC₃H₄N)₄.⁷

Synthesis and Properties of 4:1 Adducts

Addition of Lewis bases to solutions of Pd(F₆acac)₂ in solvents of low dielectric constant such as chloroform, toluene, or pentane results in successive displacement of the F₆acac groups⁸ to yield Pd(F₆acac)₂(base) (*n* = 1, 2, 3, 4). The stoichiometry of the materials isolated appears to be a function of the steric and electronic properties of the donor molecule. When the base is a strong σ donor and not highly hindered, these reactions go to completion to yield only Pd(F₆acac)₂(ligand)₄. Examples of such bases include ammonia and methylamine. The 4:1 adducts usually have low solubility in nonpolar solvents and separate from the reaction mixtures in analytical purity. Dimethylamine is a more hindered donor and generates both 1:1 and 2:1 adducts when a deficiency of amine is employed but, in the presence of excess amine, provides Pd(F₆acac)₂[(CH₃)₂NH]₄ (**1**). Heterocyclic nitrogen-containing donors such as pyridine, imidazole, and 3,5-dimethylpyrazole all afford 4:1 adducts in nearly quantitative yield. Analytical and spectroscopic data for these and other new compounds prepared are given in Tables S1-4 (supplementary material).

- (1) (a) 3M Central Research Laboratories. (b) University of Minnesota.
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As confirmed by the X-ray structure of the tetrakis(4-chloropyridine) adduct described below, the 4:1 Lewis base complexes have the general formula $(L_4Pd^{2+})(F_6acac^-)_2$. Tight ion pairing appears to occur in solution so that, for example, the osmometric molecular weight in chloroform of $(py)_4Pd-(F_6acac)_2$ (**3**) is 710 while the value calculated for an undissociated compound is 836. However, a plot of $\Lambda - \Lambda_e$ vs. $c^{1/2}$ for **3** over a concentration range of 10^{-3} – 10^{-5} M in nitromethane was linear and had a slope of 428, which is consistent with the behavior of a 2:1 electrolyte.⁹ The ionic nature of the pyridine complex in solution was confirmed by its reaction with ammonium hexafluorophosphate in methanol to produce $[(py)_4Pd](PF_6)_2$ (**8**).¹⁰

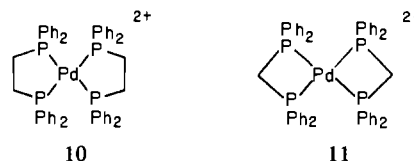
These amine and other 4:1 adducts of $Pd(F_6acac)_2$ are colorless to pale yellow. In contrast, the analogous 2:1 adducts are yellow due to an absorption maximum at about 350 nm, which extends into the visible.^{2b} This band is attributed to a $d_{xy} \rightarrow d_{x^2-y^2}$ transition, which occurs at low energy because of the presence of one covalently bonded hexafluoroacetylacetonate ligand in $[L_2Pd(F_6acac)]^+F_6acac^-$. Alkylamines, heterocyclic amines, and phosphines are expected to cause a much greater ligand field splitting than F_6acac^- , and as a result, the d–d transition in $L_4Pd(F_6acac)_2$ is shifted further into the ultraviolet.

As we reported earlier,^{2b} the reaction of *tert*-butyl isocyanide and $Pd(F_2acac)_2$ in pentane affords $Pd(F_6acac)_2(t-C_4H_9NC)_4$ (**9**). This compound decomposes on standing at room temperature but may be stored for months at $-20^\circ C$, a phenomenon that may be associated with the lack of reports of stable $Pd(RNC)_4^{2+}$ salts.¹¹ However, the silicotungstate salt does not decompose at room temperature.¹²

The ¹³C NMR spectrum of **3**, Table S-3, reveals that the pyridine carbons are deshielded by about 3 ppm relative to free pyridine, a result similar to that obtained for $[(py)_4Pt]^{2+}$.¹³ The effect of the metal on the ¹H chemical shifts is much larger. In particular, the H(2,6) protons are deshielded due to the total magnetic anisotropy associated with the tetragonal system and appear as a quartet [$J_{H(2)-H(3)} = 5$ Hz, $J_{H(2)-H(4)} = 2$ Hz] at δ 9.83 in **3** and δ 9.20 in **8**.

Chelation appears to provide a driving force for the formation of some 4:1 adducts. Thus, while only a 1:1 adduct is obtained from $Pd(F_6acac)_2$ and triphenylphosphine in chloroform or toluene,⁸ the bidentate phosphines $Ph_2PC_2H_4PPh_2$ and $Ph_2PCH_2PPh_2$ afforded $Pd(F_6acac)_2-(Ph_2PC_2H_4PPh_2)_2$ (**10**) and $Pd(F_6acac)_2-(Ph_2PCH_2PPh_2)_2$ (**11**), respectively. Similarly, while only $Pd(F_6acac)_2(Ph_3As)_2$ was isolated from the reaction of $Pd(F_6acac)_2$ with excess triphenylarsine, $Ph_2AsC_2H_4AsPh_2$ afforded $Pd(F_6acac)_2-(Ph_2AsC_2H_4AsPh_2)_2$ (**12**). Chemical evidence that **10**, **11**, and **12** are ionic chelates of the type $(L_4Pd^{2+})(F_6acac^-)_2$ comes from their reaction with methanolic ammonium hexafluorophosphate to yield respectively $[(Ph_2PC_2H_4PPh_2)_2Pd](PF_6)_2$ (**13**), $[(Ph_2PCH_2PPh_2)_2Pd](PF_6)_2$ (**14**), and $[(Ph_2AsC_2H_4AsPh_2)_2Pd](PF_6)_2$ (**15**). The ³¹P NMR chemical shifts in phosphorus chelate rings are characteristic and can be used for structural assignments.^{14,15} The [¹H]³¹P NMR spectra of **10** and **11** comprise singlets at 58.9 (i.e., downfield from H_3PO_4) and -32.6 ppm. The ³¹P NMR data show that both phosphines function as bidentate ligands, and the alter-

nation in chemical shift on going from **10** to **11** is indicative of chemically equivalent phosphorus contained in five- and four-membered rings, respectively:



Because of the small bite angle, bis(diphenylphosphino)methane usually forms bridged complexes, but chelates, e.g., $(Ph_2P)_2CH_2Pd(SCN)_2$, are also known.¹⁶ Balch¹⁷ has recently summarized structural correlations in $(Ph_2P)_2CH_2$ and $(Ph_2As)_2CH_2$ complexes. In contrast to phosphorus and arsenic donors, triphenylstibine formed a 4:1 adduct with $Pd-(F_6acac)_2$. In solution, $Pd(F_6acac)_2(Ph_3Sb)_4$ (**16**) appears to be extensively ionized and/or dissociated. The osmometric molecular weight in chloroform is 602 compared with the calculated value of 1932, and in this solvent, the ¹⁹F spectrum contains a singlet at 76.0 ppm, indicative of ionic hexafluoroacetylacetonate.

The three sulfur donors studied in this work, 1,3-dithiolene-2-thione, benzothiazole, and 1,4-dithiacyclohexane (1,4-dithiane) all formed 4:1 adducts regardless of the ligand: Pd ratio. The thioetone complex $Pd(F_6acac)_2(1,3-C_3H_2S_3)_4$ (**17**) is obtained as scarlet crystals in which the long-wavelength band in the electronic spectrum at 365 nm is attributed to ligand \rightarrow metal charge-transfer processes similar to those observed in group 6B metal carbonyl complexes of this thione.^{18,19} The ligating site in benzothiazole has not been rigorously established. However, by analogy with the phenothiazine complexes of $Pd(F_6acac)_2$, shown by X-ray photoelectron spectroscopy to contain Pd–S bonds,^{2b} the ligands in $(benzothiazole)_4Pd(F_6acac)_2$ (**18**) are likely bonded through sulfur.

The cyclic thioether 1,4-dithiane forms both 1:1 and 2:1 complexes with metal ions, and the former may be oligomeric.²⁰ Examples of complexes that have been crystallographically characterized include 1,4- $C_4H_8S_2(SbI_3)_2$ ²¹ and 1,4- $C_4H_8S_2-SbCl_3$.²² The platinum complex (1,4- $C_4H_8S_2$)- $PtCl_2$ is insoluble in common solvents and has been characterized by vibrational spectroscopy.²³ Chemical and spectroscopic data indicate that in, inter alia, $[(1,4-C_4H_8S_2)Rh(1,4-C_4H_8S_2)]PF_6$ and $[(\eta^3-RC_3H_4)Pd(1,4-C_4H_8S_2)]PF_6$, the thioether has a boatlike conformation and functions as a bidentate ligand.²⁴

Several lines of evidence indicate that in $Pd(F_6acac)_2(1,4-C_4H_8S_2)_2$ (**19**) the thioether ligand has a similar conformation and that **19** can be written as $[(\eta^2-1,4-C_4H_8S_2)_2Pd](F_6acac)_2$. The X-ray photoelectron spectra of this material and of $[(1,4-C_4H_8S_2)_2Pd](PF_6)_2$ (**20**), prepared by metathesis with ammonium hexafluorophosphate, reveal that the Pd ($3d_{5/2}$) and S (2s) core binding energies are at 388.3 and 288.5 eV, respectively (relative to C (1s) at 285.0 eV), indicating that both sulfur atoms in 1,4-dithiane are bonded to palladium. The same conclusion is reached from a consideration of the pro-

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Table I. Selected Distances and Angles within Pd(F₆acac)₂(4-ClC₅H₄N)₄^a

Distances, Å			
Pd1-N2	2.034 (5)	Pd2-N3	2.019 (5)
Pd1-N4	2.025 (5)	Pd2-N1	2.029 (4)
Pd1-O1C	3.006 (5)	Pd2-O1A	3.032 (5)
Pd1-O1D	4.473 (6)	Pd2-O1B	4.729 (6)
O1C-C12C	1.238 (7)	O1A-C12A	1.222 (8)
O1D-C12D	1.223 (9)	O1B-C12B	1.232 (9)
C12C-C11C	1.381 (9)	C12A-C11	1.39 (1)
C12D-C11C	1.40 (1)	C12B-C11	1.39 (1)
C12C-C13C	1.539 (9)	C12A-C13A	1.53 (1)
C12D-C13D	1.49 (1)	C12B-C13B	1.49 (1)
C13C-F1C	1.304 (9)	C13A-F1A	1.24 (1)
C13C-F2C	1.312 (8)	C13A-F2A	1.31 (1)
C13C-F3C	1.289 (9)	C13A-F3A	1.27 (1)
C13D-F1D	1.27 (1)	C13B-F1B	1.17 (1)
C13D-F2D	1.23 (2)	C13B-F2B	1.31 (1)
C13D-F3D	1.28 (1)	C13B-F3B	1.33 (1)
N2-C2A	1.325 (8)	N3-C3A	1.334 (8)
N2-C2E	1.333 (8)	N3-C3E	1.364 (8)
C2A-C2B	1.372 (9)	C3A-C3B	1.378 (9)
C2B-C2C	1.37 (1)	C3B-C3C	1.38 (1)
C2C-C2D	1.35 (1)	C3C-C3D	1.36 (1)
C2D-C2E	1.377 (9)	C3D-C3E	1.384 (9)
C2C-C12	1.739 (7)	C3C-C13	1.723 (7)
N4-C4A	1.361 (8)	N1-C1A	1.338 (8)
N4-C4E	1.362 (8)	N1-C1E	1.336 (8)
C4A-C4B	1.382 (9)	C1A-C1B	1.376 (9)
C4B-C4C	1.39 (1)	C1B-C1C	1.38 (1)
C4C-C4D	1.38 (1)	C1C-C1D	1.33 (1)
C4D-C4E	1.35 (1)	C1D-C1E	1.397 (9)
C4C-C14	1.743 (7)	C1C-C11	1.730 (7)
Angles, Deg			
N2-Pd1-N4	89.7 (2)	Pd1-N2-C2A	120.0 (4)
N2-Pd1-N4' ^b	90.3 (2)	Pd1-N2-C2E	120.8 (4)
N2-Pd1-O1C	89.3 (2)	Pd1-N4-C4A	119.4 (4)
N2-Pd1-O1C'	90.7 (2)	Pd1-N4-C4E	122.0 (5)
N4-Pd1-O1C	90.4 (2)	N1-Pd2-N3	88.9 (2)
N4-Pd1-O1C'	89.6 (2)	N1-Pd2-N3'	91.1 (2)
O1C-C12C-C11C	130.4 (6)	N3-Pd2-O1A	86.9 (2)
C12C-C11C-C12D	123.4 (6)	N3-Pd2-O1A'	93.1 (2)
C11C-C12D-O1D	129.3 (7)	N1-Pd2-O1A	92.4 (2)
		N1-Pd2-O1A'	87.6 (2)
		O1A-C12A-C11	128.6 (7)
		C12A-C11-C12B	124.4 (7)
		C11-C12B-O1B	128.5 (8)
		Pd2-N1-C1A	121.0 (4)
		Pd2-N1-C1E	119.4 (5)
		Pd2-N3-C3A	120.2 (4)
		Pd2-N3-C3E	121.0 (4)

^a The number in parentheses is the estimated standard deviation in the last significant figure. ^b Primed atoms are related to unprimed atoms by an inversion operation through the Pd atom.

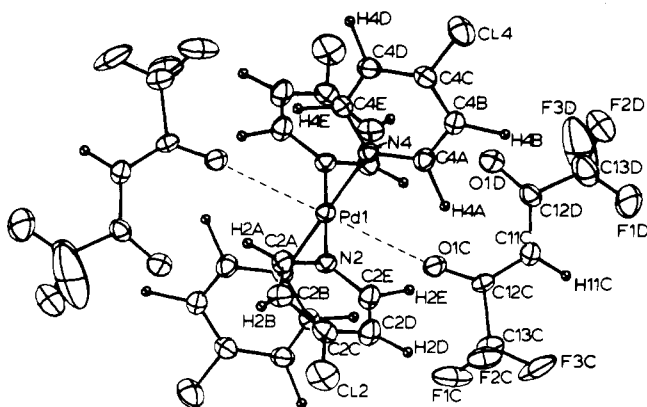
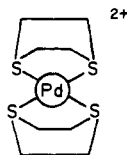


Figure 1. ORTEP drawing of the Pd1 molecule using 30% probability ellipsoids. The Pd atom is at an inversion center.

ton-decoupled ¹³C NMR spectrum of **19**, which shows a single resonance at 36.3 ppm due to the dithiane ring methylene carbons. By analogy with the published spectra of (1,4-C₄H₈S₂)PtX₂,¹⁹ Raman bands in **19** and **20** at 389 and 417 cm⁻¹ are attributed to ring bending modes and those at 307 and 634 cm⁻¹ to Pd-S and C-S stretching, respectively. The strong bands of PF₆⁻ salt match those of the hexafluoroacetylacetonate analogue, both in the solid state and in methanol solution, suggesting that changing counterions has little effect on the gross structure of the [(1,4-C₄H₈S₂)₂Pd]²⁺ core. Further, there is a lack of coincidence between the Raman and infrared spectra of **20**, which we interpret to mean that the [(1,4-C₄H₈S₂)₂Pd]²⁺ ion has a centrosymmetric structure:



In order to further characterize the Pd(F₆acac)₂L₄ class of compounds, an X-ray crystal structure determination on Pd-

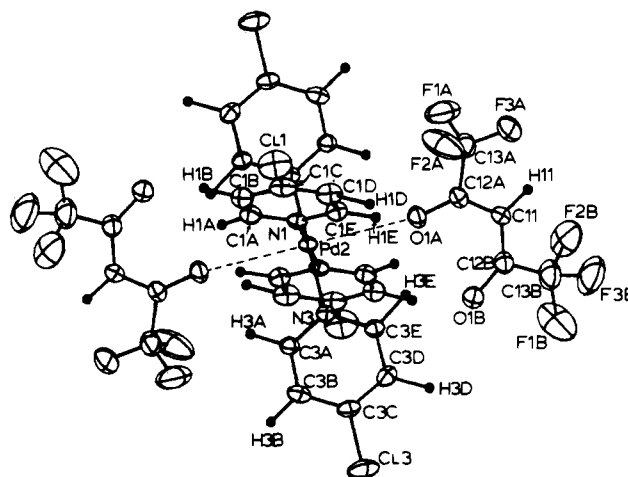


Figure 2. ORTEP drawing of the Pd2 molecule using 30% probability ellipsoids. The Pd atom is at an inversion center.

(F₆acac)₂(4-ClC₅H₄N)₄ was carried out.

Description of the Structure

The two crystallographically independent Pd(F₆acac)₂(4-ClC₅H₄N)₄ molecules contain inversion centers of symmetry at their Pd atom positions (Figures 1 and 2). The molecules are well separated in space with no unusually short intermolecular distances. A tabulation of selected intramolecular distances and angles is presented in Table I. It is seen that displacement of both fluorinated β-diketonate ligands has occurred. Both molecules have coordination cores that are comprised of palladium and four nitrogen atoms from the chloropyridine ligands. The PdN₄ group is crystallographically required to be planar. The planes of the pyridine rings are approximately perpendicular to the PdN₄ plane (Table II) and *d*(Pd-N)_{av} is 2.027 Å, in close agreement with 2.038 Å in [(bpy)₂Pd(H₂O)₂](NO₃)₂.²⁵ Two oxygen atoms, one from each F₆acac, occupy axial positions, in what may be described

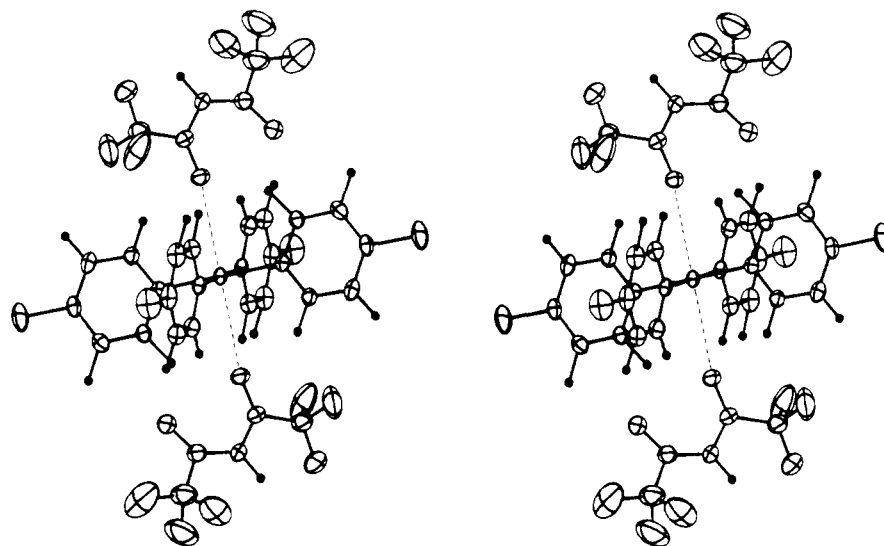


Figure 3. ORTEP stereoview of the Pd1 molecule. The Pd2 molecule has a similar geometry and is not shown.

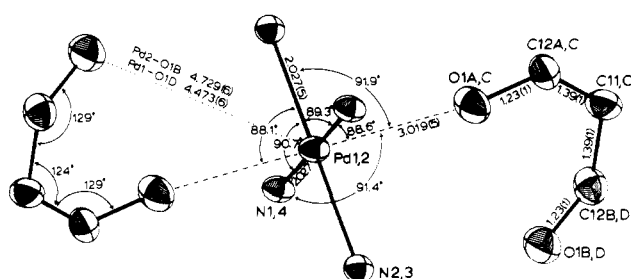


Figure 4. ORTEP drawing of the PdN₄O₂ coordination core with selected distances (Å) and angles (deg). Distances and angles are averages for the two unique molecules except for the Pd distances to O1B and O1D, which are quite different. All averages are within 5σ of the actual values. The Pd is at an inversion center.

as a grossly tetragonally distorted octahedral coordination geometry, with long (3.02 Å) palladium–oxygen contacts. Figure 3 shows an ORTEP stereoview of the Pd2 molecule, and an ORTEP drawing of the coordination core with selected distances and angles is presented in Figure 4. It is apparent that the distances and angles within the cores of the two independent molecules are quite similar (Figure 4 and Table I). These chemically equivalent distances and angles are within 5σ, except for the longer Pd–O1B and –O1D distances, which differ by 0.25 Å. The distances and angles shown in Figure 4 have been averaged over the two independent molecules.

Both hexafluoroacetylacetonate groups display similar distances and angles. Within each of these moieties, the C–O and C(methine)–C(carbonyl) distances are also similar and indicative of a delocalized, symmetrical enolate structure, in contrast to the alternating bond lengths found in the bis-(pyridine) complexes of copper and zinc hexafluoroacetylacetonates.²⁶ The backbone of the F₆acac group containing O1C and O1D is planar with a maximum atomic displacement from the least-squares plane of 0.01 Å (Table II, plane 7). The other, however, containing O1A and O1B is slightly twisted about the C(11)–C12A and –C12B bonds so that O1A and O1B are 0.04 Å below and above the least-squares plane, respectively.

Experimental Section

Infrared spectra were obtained as Nujol mulls on an instrument with grating optics; frequencies of peak maxima are believed to be accurate to within ±5 cm⁻¹. Ultraviolet spectra were recorded on a Cary 14 spectrometer. A Varian XL-100 spectrometer was used

to obtain NMR spectra; internal (CH₃)₄Si or CFCl₃ and external H₃PO₄ were employed as references. Raman spectra were recorded on a Spex Ramalog instrument equipped with spinning sample holders. The conductivity measurements were made with a dip type cell having platinumized electrodes.

[(CH₃)₂NH]₄Pd(F₆acac)₂ (1). A stream of dry dimethylamine was passed through a solution of 0.3 g of Pd(F₆acac)₂ in 7 mL of pentane. Yellow crystals of [(CH₃)₂NH]₄Pd(F₆acac)₂ began to separate. The flow of amine was continued until white crystals of **1** precipitated; mp 137–139 °C dec. The product was collected on a filter, washed with pentane, and air-dried. The yield was 0.3 g (75%).

(py)₄Pd(F₆acac)₂ (3). To 0.19 g of Pd(F₆acac)₂ in 10 mL of pentane was added 0.5 mL of pyridine. The white solids that formed were recrystallized from methylene chloride–hexane to give 0.20 g (66%) of **3** as white needles, mp 193 °C dec.

[(py)₄Pd](PF₆)₂ (8). Methanolic ammonium hexafluorophosphate was added to 0.65 g of **3** dissolved in 5 mL of warm methanol. Recrystallization of the resulting white precipitate from acetone–methanol gave 0.4 g (73%) of white crystalline product.

(Ph₂PC₂H₄PPh₂)₂Pd(F₆acac)₂ (10). To 0.80 g of Ph₂PC₂H₄PPh₂ (2 mmol) in 10 mL of benzene was added with stirring 0.52 g (1 mmol) of Pd(F₆acac)₂ in 5 mL of the same solvent. The product separated as granular white solids, which were collected on a filter, washed with fresh solvent, and vacuum-dried. The yield was 1.25 g (95%). An analytical sample was obtained by recrystallization from acetone–ethanol; mp 212–213 °C.

(Ph₃Sb)₄Pd(F₆acac)₂ (16). A solution of 0.38 g (1.1 mmol) of Ph₃Sb in 10 mL of warm hexane was added with stirring to 0.13 g (0.25 mmol) of Pd(F₆acac)₂ in 3 mL of hexane. The reaction mixture was concentrated with a nitrogen jet to ca. 8 mL. The pale yellow crystalline product was then collected on a filter and vacuum-dried. The yield was 0.16 g (33%). The X-ray powder pattern was unique and did not show lines due to the starting materials.

(1,4-C₄H₈S₂)₂Pd(F₆acac)₂ (19). A solution of 0.26 of Pd(F₆acac)₂ in 5 mL of pentane was added to a solution of 0.13 g of 1,4-C₄H₈S₂ in 20 mL of pentane. The pale yellow crystalline product, mp 187 °C, was collected on a filter and then vacuum-dried. The yield was 0.31 g (82%). Raman spectrum (6265-Å excitation): 2475 (w), 1550 (m), 1315 (s), 1065 (s), 940 (w), 740 (m), 665 (m), 640 (s), 470 (m), 395 (vs), 310 (s), 350 (s) cm⁻¹.

[(1,4-C₄H₈S₂)₂Pd](PF₆)₂ (20). Excess methanolic NH₄PF₆ was added to a yellow solution of 0.76 g (1 mmol) of **19**, in 6 mL of methanol. The solids that separated were recrystallized by slow evaporation of an acetone–ethanol solution to give 0.52 g of **20** (82%) as light yellow microcrystals. Raman spectrum (6265-Å excitation): 2950 (w), 1425 (w), 974 (w), 741 (s), 660 (w), 634 (s), 417 (s), 389 (vs), 307 (s). X-ray photoelectron spectrum (relative to C(1s) = 285.0 eV): Pd(3d_{5/2}), 388.3; S(2s), 228.5 eV.

Structure Determination. Since good crystals of Pd(F₆acac)₂(py)₄ were not obtained, synthesis of a substituted derivative was undertaken. 4-Chloropyridine was prepared by neutralization of the commercially available hydrochloride salt with aqueous sodium hydroxide. The

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

Table II

Least-Squares Planes ^a									
plane no.	A	B	C	D	atom	x	y	z	dist, Å
1	-0.8877	-0.4558	-0.0658	0.0000	Pd1 ^b	0.0000	0.0000	0.0000	0.000
					N2 ^b	0.1391	-0.5527	1.9526	-0.000
					N4 ^b	-0.9213	1.7131	0.5617	0.000
2	-0.1662	-0.9784	-0.1232	-1.6089	Pd2 ^b	9.6781	0.0000	0.0000	0.000
					N1 ^b	8.6002	-0.0333	1.7190	0.000
					N3 ^b	11.3350	-0.4169	1.0753	0.000
3	0.5086	-0.8133	-0.2826	-0.0449	N2 ^b	0.1391	-0.5527	1.9526	0.013
					C2A ^b	-0.8041	-1.3083	2.4958	-0.005
					C2B ^b	-0.7514	-1.7286	3.8007	-0.005
					C2C ^b	0.3255	-1.3317	4.5489	0.008
					C2D ^b	1.2840	-0.5383	4.0196	-0.000
					C2E ^b	1.1609	-0.1456	2.7052	-0.011
					Pd1 ^c	0.0000	0.0000	0.0000	0.045
					Cl2 ^c	0.4389	-1.8654	6.2000	0.033
4	0.0854	0.4442	-0.8918	0.1958	N4 ^b	-0.9213	1.7131	0.5617	-0.015
					C4A ^b	-0.1837	2.7202	1.1048	0.011
					C4B ^b	-0.7722	3.8574	1.6247	0.003
					C4C ^b	-2.1573	3.9466	1.5547	-0.014
					C4D ^b	-2.9123	2.9537	0.9610	0.010
					C4E ^b	-2.2731	1.8643	0.4872	0.004
					Pd1 ^c	0.0000	0.0000	0.0000	-0.196
					Cl4 ^c	-2.9402	5.3269	2.2755	-0.110
5	0.5036	-0.1612	-0.8488	4.8586	N3 ^b	11.3350	-0.4169	1.0753	0.004
					C3A ^b	11.5788	-1.6654	1.4764	-0.013
					C3B ^b	12.7058	-2.0187	2.1871	0.009
					C3C ^b	13.5862	-1.0114	2.5234	0.004
					C3D ^b	13.3497	0.2767	2.1587	-0.013
					C3E ^b	12.2743	0.5697	1.4385	0.009
					Pd2 ^c	9.6781	0.0000	0.0000	0.015
					Cl3 ^c	15.0213	-1.4034	3.3918	0.053
6	-0.7529	0.4350	-0.4938	-7.3407	N1 ^b	8.6002	-0.0333	1.7190	0.002
					C1A ^b	7.8089	-1.0700	2.0157	0.000
					C1B ^b	7.0440	-1.1042	3.1588	0.003
					C1C ^b	7.1102	-0.0175	4.0009	0.004
					C1D ^b	7.8978	1.0166	3.7223	-0.002
					C1E ^b	8.6609	1.0096	2.5519	-0.001
					Pd2 ^c	9.6781	0.0000	0.0000	0.054
					Cl1 ^c	6.1403	0.0092	5.4326	0.039
7	0.4189	-0.3879	-0.8210	0.4168	O1C ^b	2.6807	1.3401	0.2265	0.000
					C12C ^b	3.6846	2.0405	0.4137	-0.004
					C11C ^b	3.9903	3.3071	-0.0443	0.008
					C12D ^b	3.1193	4.0743	-0.8303	-0.009
					O1D ^b	2.0160	3.7849	-1.2724	0.004
					C13C ^c	4.7285	1.3419	1.3032	-0.026
C13D ^c	3.5918	5.4335	-1.2138	-0.023					
8	-0.2806	0.1259	-0.9515	-5.1449	O1A ^b	8.1729	12.3744	4.6717	-0.035
					C12A ^b	8.1329	13.5924	4.7653	0.041
					C11 ^b	7.0938	14.3925	5.2178	0.002
					C12B ^b	5.8364	13.9198	5.5745	-0.044
					O1B ^b	5.3985	12.7762	5.4711	0.036
					C13A ^c	9.4158	14.3413	4.3889	0.133
C13B ^c	4.8526	14.8809	6.1537	-0.198					

Dihedral Angles between Planes

plane no.	plane no.	dihedral angle, deg	plane no.	plane no.	dihedral angle, deg
1	3	86	2	6	76
1	4	77	2	8	88
1	7	82	3	4	86
2	5	80	5	6	88

^a Planes were calculated with use of unit weights. The equation of the plane is of the form $Ax + By + Cz - D = 0$, where A , B , C , and D are constants and x , y , and z are orthogonalized coordinates. ^b Atoms in the plane. ^c Other atoms.

free base was isolated by extraction into methylene chloride, followed by evaporation. A solution of 2.0 mmol of 4-chloropyridine in 3 mL of benzene was added to 0.26 g (0.5 mmol) of Pd(F₆acac)₂ in 2 mL

of the same solvent. Octane was added to induce the precipitation of fine white needles of Pd(F₆acac)₂(4-ClC₅H₄N)₄, mp 187 °C dec. Anal. Calcd: C, 37.0; H, 1.8; N, 5.7. Found: C, 36.7; H, 1.6; N,

Table III. 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
Pd1	0.0000 (0)	0.0000 (0)	0.0000 (0)	4.16 (3)	4.34 (3)	3.29 (2)	-0.01 (3)	0.22 (2)	0.45 (3)
Pd2	0.5000 (0)	0.0000 (0)	0.0000 (0)	3.39 (2)	4.53 (3)	3.49 (2)	0.64 (3)	1.02 (2)	0.00 (3)
Cl2	0.0798 (2)	-0.0987 (2)	0.5921 (2)	13.0 (2)	11.0 (2)	4.16 (8)	0.4 (2)	0.6 (1)	2.7 (1)
Cl4	-0.1309 (1)	0.2818 (1)	0.2173 (3)	8.9 (1)	6.1 (1)	12.9 (1)	0.7 (1)	5.4 (1)	-1.2 (1)
Cl1	0.3673 (1)	0.0005 (2)	0.5188 (2)	10.9 (1)	15.3 (2)	5.38 (8)	1.2 (2)	4.75 (7)	0.6 (1)
Cl3	0.8073 (1)	-0.0742 (2)	0.3239 (2)	5.2 (1)	13.5 (2)	7.7 (1)	2.3 (1)	-1.7 (1)	-1.2 (1)
F1A	0.5816 (3)	0.7516 (4)	0.4977 (8)	6.8 (3)	18.3 (5)	23.2 (6)	-3.1 (3)	-0.8 (4)	9.8 (4)
F2A	0.5445 (4)	0.7301 (4)	0.3173 (7)	20.3 (4)	15.7 (5)	19.4 (4)	-9.7 (4)	14.0 (3)	-6.9 (4)
F3A	0.5208 (3)	0.8242 (3)	0.3933 (7)	10.1 (3)	6.7 (3)	19.7 (5)	-0.9 (3)	5.1 (3)	3.6 (3)
F1B	0.2566 (3)	0.7676 (5)	0.6227 (8)	23.8 (3)	14.1 (6)	45.3 (6)	-4.7 (4)	29.2 (3)	-8.2 (5)
F2B	0.3409 (4)	0.8316 (4)	0.6720 (6)	14.2 (5)	16.3 (4)	14.6 (4)	4.1 (4)	0.8 (4)	-9.1 (3)
F3B	0.2827 (5)	0.8379 (5)	0.5052 (9)	14.4 (5)	16.4 (5)	22.8 (7)	7.2 (4)	2.9 (5)	-3.9 (5)
F1C	0.2667 (3)	0.0075 (3)	0.0835 (6)	11.1 (3)	12.2 (3)	8.8 (3)	7.5 (2)	-0.2 (3)	-0.9 (3)
F2C	0.2452 (2)	0.0617 (3)	0.2416 (4)	6.7 (2)	12.1 (3)	4.7 (2)	3.1 (2)	0.8 (2)	1.6 (2)
F3C	0.3159 (3)	0.1021 (4)	0.1288 (6)	3.5 (2)	21.3 (5)	16.4 (4)	-0.8 (3)	-1.4 (3)	10.1 (4)
F1D	0.2344 (4)	0.3108 (4)	-0.0656 (9)	10.9 (4)	11.6 (4)	27.8 (7)	-5.0 (3)	-2.8 (5)	9.5 (4)
F2D	0.1351 (5)	0.3369 (4)	-0.1029 (10)	17.0 (6)	6.6 (4)	32 (1)	-0.4 (4)	-6.2 (7)	1.4 (5)
F3D	0.1676 (7)	0.2926 (4)	-0.2374 (7)	49 (1)	14.5 (5)	12.0 (4)	-13 (5)	9.4 (5)	3.5 (3)
O1C	0.1406 (3)	0.0709 (3)	0.0216 (5)	4.6 (2)	6.3 (3)	7.4 (3)	-0.2 (2)	0.0 (2)	1.9 (2)
O1D	0.0924 (3)	0.2002 (3)	-0.1215 (6)	6.8 (3)	6.8 (3)	11.4 (4)	-0.2 (3)	-0.7 (3)	2.9 (3)
O1A	0.4653 (3)	0.6547 (3)	0.4462 (5)	6.3 (2)	4.3 (2)	10.0 (3)	0.3 (2)	3.1 (2)	-0.2 (2)
O1B	0.3289 (3)	0.6759 (3)	0.5225 (6)	6.2 (3)	6.0 (3)	10.8 (4)	0.1 (2)	2.5 (3)	1.0 (3)
N2	0.0252 (3)	-0.0292 (3)	0.1865 (5)	4.2 (2)	4.9 (2)	3.2 (2)	0.1 (2)	0.2 (2)	0.8 (2)
N4	-0.0424 (3)	0.0906 (3)	0.0536 (5)	4.0 (2)	4.5 (3)	4.0 (2)	0.2 (2)	0.6 (2)	0.5 (2)
N1	0.4602 (3)	-0.0018 (3)	0.1642 (5)	3.9 (2)	4.7 (2)	3.5 (2)	1.1 (2)	1.0 (2)	0.1 (2)
N3	0.5955 (3)	-0.0221 (3)	0.1027 (5)	4.0 (2)	4.4 (2)	3.3 (2)	0.5 (2)	0.8 (2)	-0.2 (2)
C2D	0.1034 (5)	-0.0285 (5)	0.3839 (7)	7.0 (4)	7.4 (4)	4.2 (3)	-2.0 (4)	-0.9 (3)	0.9 (3)
C2E	0.0849 (4)	-0.0077 (4)	0.2584 (7)	6.1 (4)	6.3 (4)	4.0 (3)	-1.6 (3)	-0.3 (3)	0.9 (3)
C2A	-0.0185 (4)	-0.0692 (4)	0.2384 (7)	5.0 (3)	5.6 (4)	5.0 (3)	-0.4 (3)	1.1 (3)	0.8 (3)
C4A	0.0007 (4)	0.1439 (4)	0.1055 (7)	4.3 (3)	5.5 (4)	6.2 (4)	-0.2 (3)	1.4 (3)	-0.9 (3)
C4B	-0.0249 (4)	0.2041 (4)	0.1552 (7)	5.0 (3)	5.2 (4)	6.6 (4)	-0.6 (3)	0.7 (3)	-0.4 (3)
C4C	-0.0971 (4)	0.2088 (4)	0.1485 (7)	5.7 (3)	4.7 (3)	6.0 (3)	0.7 (3)	1.9 (3)	0.7 (3)
C4D	-0.1416 (4)	0.1563 (4)	0.0918 (7)	4.9 (3)	5.3 (4)	6.5 (4)	0.9 (3)	1.1 (3)	1.0 (3)
C4E	-0.1129 (4)	0.0986 (4)	0.0465 (7)	5.1 (3)	4.6 (3)	6.5 (4)	-0.1 (3)	0.7 (3)	0.9 (3)
C1D	0.4423 (4)	0.0538 (5)	0.3555 (6)	6.5 (4)	8.9 (5)	3.4 (3)	1.3 (4)	1.3 (3)	-0.4 (3)
C1E	0.4710 (4)	0.0534 (4)	0.2437 (6)	5.0 (3)	6.1 (4)	3.7 (3)	0.4 (3)	1.2 (2)	-0.6 (3)
C3A	-0.3882 (3)	-0.0881 (4)	0.1410 (7)	4.3 (3)	4.9 (3)	5.0 (3)	0.6 (3)	0.9 (3)	-0.2 (3)
C3B	-0.3234 (4)	-0.1068 (4)	0.2089 (7)	5.5 (3)	6.1 (4)	5.6 (4)	2.1 (3)	0.1 (3)	0.5 (3)
C3C	0.7252 (3)	-0.0535 (4)	0.2410 (6)	3.8 (3)	7.2 (4)	4.3 (3)	1.1 (3)	0.8 (2)	-0.7 (3)
C3D	-0.2904 (4)	0.0146 (4)	0.2062 (7)	4.5 (3)	6.7 (4)	5.3 (3)	-0.8 (3)	1.0 (3)	-1.4 (3)
C3E	-0.3562 (4)	0.0301 (4)	0.1374 (6)	4.2 (3)	5.3 (3)	4.3 (3)	0.2 (3)	0.9 (2)	-0.2 (3)
C13A	0.5269 (5)	0.7587 (5)	0.4192 (9)	7.8 (4)	5.6 (4)	10.2 (5)	0.4 (4)	4.1 (4)	0.7 (4)
C12A	0.4641 (4)	0.7191 (4)	0.4551 (7)	6.2 (4)	4.1 (3)	6.3 (4)	-0.1 (3)	1.2 (3)	0.5 (3)
C11	0.4146 (4)	0.7614 (4)	0.4983 (8)	4.9 (3)	4.4 (3)	8.5 (5)	-0.8 (3)	0.8 (3)	-0.8 (3)
C12B	0.3529 (4)	0.7364 (4)	0.5324 (7)	6.4 (4)	5.2 (4)	6.3 (4)	0.4 (3)	1.7 (3)	0.1 (3)
C13B	0.3074 (6)	0.7873 (6)	0.5877 (11)	11.0 (6)	7.8 (6)	12.3 (6)	2.3 (5)	4.5 (5)	-0.0 (5)
C13C	0.2563 (4)	0.0710 (5)	0.1245 (7)	4.6 (3)	8.0 (5)	6.1 (4)	1.3 (3)	1.1 (3)	1.2 (4)
C12C	0.1942 (3)	0.1080 (4)	0.0395 (6)	3.0 (3)	6.0 (4)	4.7 (3)	0.6 (3)	0.8 (2)	0.3 (3)
C11C	0.2057 (4)	0.1750 (4)	-0.0042 (6)	5.1 (3)	5.4 (4)	4.8 (3)	-1.1 (3)	0.6 (3)	0.1 (3)
C12D	0.1535 (4)	0.2156 (4)	-0.0793 (7)	6.7 (4)	4.5 (3)	4.9 (3)	0.1 (3)	0.6 (3)	0.9 (3)
C13D	0.1744 (7)	0.2875 (5)	-0.1159 (9)	14.2 (8)	6.7 (5)	8.5 (5)	-1.4 (6)	0.2 (6)	2.3 (4)
C2B	-0.0038 (4)	-0.0915 (4)	0.3630 (6)	5.9 (4)	6.7 (4)	4.4 (3)	0.7 (3)	1.8 (3)	1.7 (3)
C2C	0.0588 (4)	-0.0705 (4)	0.4344 (6)	7.5 (4)	5.4 (4)	3.8 (3)	0.8 (3)	0.8 (3)	0.6 (3)
C1A	0.4220 (4)	-0.0566 (4)	0.1925 (6)	5.1 (3)	5.7 (4)	4.6 (3)	0.7 (3)	1.6 (2)	0.4 (3)
C1B	0.3930 (4)	-0.0584 (4)	0.3017 (7)	5.9 (4)	6.4 (4)	5.3 (3)	0.5 (3)	1.4 (3)	0.9 (3)
C1C	0.4042 (4)	-0.0009 (5)	0.3821 (6)	5.6 (3)	9.2 (5)	4.1 (3)	2.2 (4)	2.2 (2)	1.8 (3)

atom ^b	x	y	z	atom ^b	x	y	z
H1A	-0.418 (4)	0.402 (4)	0.368 (7)	H3B	0.308 (4)	0.160 (4)	-0.269 (7)
H1B	-0.357 (4)	0.399 (4)	0.189 (7)	H3D	-0.251 (4)	0.061 (4)	0.246 (7)
H1D	-0.479 (4)	0.597 (4)	0.063 (7)	H3E	-0.378 (4)	0.409 (4)	0.596 (7)
H1E	-0.496 (4)	0.100 (4)	0.213 (7)	H4A	0.068 (4)	0.130 (4)	0.106 (7)
H2A	-0.056 (4)	-0.093 (4)	0.175 (7)	H4B	0.019 (4)	0.248 (4)	0.205 (7)
H2B	-0.017 (4)	-0.116 (4)	0.424 (7)	H4D	-0.200 (4)	0.170 (4)	0.043 (7)
H2D	0.147 (5)	-0.003 (4)	0.433 (8)	H4E	-0.142 (4)	0.051 (4)	0.026 (7)
H2E	0.116 (4)	0.036 (4)	0.208 (7)	H11	-0.430 (4)	0.188 (4)	0.487 (7)
H3A	0.426 (4)	0.129 (4)	-0.094 (7)	H11C	0.254 (4)	0.196 (5)	0.019 (7)

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

^b For all H atoms $B = 6.0000 (0) \text{ \AA}^2$.

5.7. If the needle crystals were not collected quickly and, instead, the reaction mixture was allowed to stand overnight, the product consisted of clear, pale yellow cube-shaped crystals of a second polymorph, mp 190 °C dec. Anal. Found: C, 37.4; H, 1.8; N, 5.7. The infrared spectra of both polymorphs were the same but the X-ray powder diffraction pattern of each was unique. The cubic crystals

were used in the structure determination.

A crystal of $\text{Pd}(\text{F}_6\text{acac})_2(4\text{-ClC}_5\text{H}_4\text{N})_4$, $\text{PdCl}_4\text{F}_{12}\text{O}_4\text{N}_4\text{C}_{34}\text{H}_{18}$ (formula weight = 974.7), of approximate dimensions $0.35 \times 0.25 \times 0.20$ mm was selected and used in the structure determination. The crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD4-SDP peak search, centering, and indexing computer

programs.²⁷ The space group $P2_1/c$ (No. 14) was chosen from the systematic absences observed during data collection and was verified by successful solution and refinement (vide infra). A Delaunay reduction calculation (PROGRAM TRACER)²⁷ did not indicate a higher order space group. The unit cell dimensions were determined by least-squares refinement of the angular settings of 25 peaks (Mo $K\alpha$ radiation, $\lambda = 0.71069 \text{ \AA}$) centered on the diffractometer and are $a = 19.356(3) \text{ \AA}$, $b = 18.902(3) \text{ \AA}$, $c = 10.636(2) \text{ \AA}$, $\beta = 100.12(1)^\circ$, and $V = 3831 \text{ \AA}^3$. The density is calculated to be 1.690 g cm^{-3} with the assumption of $Z = 4$.

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 a variable rate ω - 2θ 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 $1\frac{1}{2}$ hours of X-ray exposure and no decay with time was noted. The intensities of 7506 ($\pm h, +k, +l$ quadrant) unique reflections were measured at room temperature in the range $2\theta = 0$ - 52° with use of graphite-monochromated Mo $K\alpha$ radiation and a variable-rate ω - 2θ scan technique. After correction for Lorentz, polarization, and background effects (but not for absorption, $\mu = 8.24 \text{ cm}^{-1}$),²⁸ 3510 reflections were judged observed [$F_o^2 \geq 2.0\sigma(F_o^2)$] and were used in all subsequent calculations.²⁷

Conventional heavy-atom techniques were used to solve the structure, and refinement, with all nonhydrogen atoms thermally anisotropic and hydrogen atoms thermally isotropic by full-matrix least-squares methods (499 variables), converged R and R_w to their

final values of 0.047 and 0.067, respectively.²⁹ The error in an observation of unit weight was determined to be 1.35 by using a value of 0.04 for p in the $\sigma(I)$ equation. Hydrogen atom positional parameters were located by difference Fourier analysis and were included in the refinement but with fixed thermal parameters. The final difference Fourier map did not reveal any chemically significant features.

The final atomic coordinates with their esd's and the final thermal parameters are given in Table III. Tables of observed and calculated structure factor amplitudes are available as supplementary material.

The unit cell of Pd(F₆acac)₂(4-ClC₅H₄N)₄ contains two crystallographically independent molecules. The two palladium atoms, Pd1 and Pd2, are located on special position 0, 0, 0 and $1/2, 0, 0$ and therefore are at inversion centers of symmetry. Figures 1 and 2 show ORTEP drawings of the two independent molecules with labeling schemes.

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Registry No. 1, 79534-29-5; 2, 65353-59-5; 3, 65353-63-1; 4, 65353-60-8; 5, 79534-31-9; 6, 79534-32-0; 7, 79534-34-2; 8, 39003-77-5; 9, 78149-17-4; 10, 79534-35-3; 11, 79534-37-5; 12, 79550-18-8; 13, 74525-12-5; 14, 79534-38-6; 15, 79550-19-9; 16, 79550-21-3; 17, 79534-40-0; 18, 79534-42-2; 19, 79550-22-9; 20, 79534-44-4; Pd(F₆acac)₂, 64916-48-9; Pd(F₆acac)₂(4-ClC₅H₄N)₄, 79534-46-6.

Supplementary Material Available: Tables of structure factor amplitudes, analytical data, and vibrational, NMR, and electronic spectral properties (22 pages). Ordering information is given on any current masthead page.

(27) 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 in Crystallography", H. Schenk, R. Olthof-Hazekamp, R. van Koningsveld, and G. C. Bassi, Eds., Delft University Press, Delft, Holland, 1978, pp 64-71.

(28) Intensity data were processed as described in "CAD4 and SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity I is given by $I = (K/NPI)(C - 2B)$ 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 $\sigma^2(I) = (K/NPI)^2[C + 4B + (pI)^2]$ 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 $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$.

(29) 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.