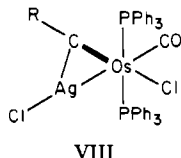


type $\text{Os}(\text{AgCl})(\text{CR})(\text{Cl})(\text{CO})(\text{PPh}_3)_2$ for which structure VIII has been determined from an X-ray diffraction study.²⁹



Here the Os-CR linkage is now 1.839 (5) Å as compared to 1.77 (2) Å found in the parent carbyne complex.²⁸ While Roper et al.²⁹ consider species VIII to be a dimetalacyclopentene complex,²⁹ we would prefer it to be considered as a carbyne complex.

Stone and co-workers³⁰ have found that platinum(0) complexes will also interact with tungsten carbynes, and a structural study of the derived species $\text{W}[(\text{CR})\text{Pt}(\text{PMe}_2\text{Ph})_2](\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2$ has been carried out. The W≡C linkage increases from 1.82 (2) Å in the parent carbyne complex¹⁰ to 1.96 Å in the platinated derivative. Here, the tungsten-platinum interaction appears sufficiently strong as to suggest consideration of the product as the dimetalacyclopentene derivative.

Clearly, the chemistry of transition-metal alkylidynes (or, more generally, carbyne complexes) is only beginning. We are in the process of studying a wide variety of aluminated metal-alkylidyne complexes, and our results will be reported in subsequent publications.

Acknowledgment. We thank Professor R. R. Schrock for providing the samples and the National Science Foundation for their financial support (Grants CHE79-24560 and CHE80-23448 to M.R.C.).

Registry No. $\text{W}(\equiv\text{CH})(\text{Cl})(\text{PMe}_3)_4$, 76642-46-1; $\text{W}(\equiv\text{CH}\cdot\text{AlMe}_2\text{Cl})(\text{Cl})(\text{PMe}_3)_3$, 76642-47-2; $\text{W}(\equiv\text{CH}\cdot\text{AlMeCl}_2)(\text{Cl})(\text{PMe}_3)_3$, 78420-99-2.

Supplementary Material Available: Listings of observed and calculated structure factor amplitudes for the two complexes (39 pages). Ordering information is given in any current masthead page.

(29) Clark, G. R.; Cochrane, C. M.; Roper, W. R.; Wright, L. J. *J. Organomet. Chem.* **1980**, *199*, C35-C38.

(30) Ashworth, T. V.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1979**, 42.

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2:1 Lewis Base Adducts of Palladium Bis(hexafluoroacetylacetonate). Structure and β -Diketonate Exchange in $(\text{bpy})\text{Pd}(\text{C}_5\text{HF}_6\text{O}_2)_2$

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Palladium bis(hexafluoroacetylacetonate), $\text{Pd}(\text{F}_6\text{acac})_2$, forms 2:1 complexes of the type $\text{Pd}(\text{F}_6\text{acac})_2\cdot 2\text{L}$ with molecular Lewis bases where $\text{L} = \text{Ph}_3\text{As}$, $1/2 (\text{Ph}_2\text{As})_2\text{CH}_2$, $(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{NH}$, $t\text{-C}_4\text{H}_9\text{NC}$, phenothiazine, phenoselenazine, $1/2$ bipyridyl, and $1/2$ tetrathianaphthacene. These compounds are ionic and may be represented as $[\text{L}_2\text{Pd}(\text{F}_6\text{acac})]^+\text{F}_6\text{acac}^-$. Variable-temperature ^{19}F NMR spectra of $[(\text{bpy})\text{Pd}(\text{F}_6\text{acac})]\text{F}_6\text{acac}$ demonstrated a rapid interconversion between the ionic and coordinated F_6acac groups with $\Delta H = 10.4 \pm 1$ kcal/mol and $\Delta S = -11 \pm 4$ eu. The bipyridyl complex crystallizes in space group $P2_1/c$ with $a = 11.991$ (5) Å, $b = 9.295$ (4) Å, $c = 21.008$ (9) Å, $\beta = 101.32$ (2)°, and $V = 2305$ Å³. A structure solution based on 1526 observed reflections converged at $R = 0.057$ and $R_w = 0.063$. The $(\text{bpy})\text{Pd}(\text{F}_6\text{acac})^+$ units are essentially planar and pack in a slipped-stack arrangement; $d(\text{Pd}-\text{N})_{av}$ is 1.987 (8) Å and $d(\text{Pd}-\text{O})_{av}$ is 2.005 (7) Å.

Introduction

The acid-base chemistry of palladium bis(hexafluoroacetylacetonate), $\text{Pd}(\text{F}_6\text{acac})_2$, is extensive in scope. This fluorinated metalloorganic forms adducts with molecular Lewis bases, which may be grouped into four broad classes, $\text{Pd}(\text{F}_6\text{acac})_2\cdot n\text{L}$ ($\text{L} = \text{base}$, $n = 1, 2, 3, 4$), according to their stoichiometry. Previously,¹ we described the members of the $n = 1$ class. This work reports the synthesis and properties of the 2:1 adducts, $\text{Pd}(\text{F}_6\text{acac})_2\cdot 2\text{L}$, and describes the crystal structure of a representative member, $\text{Pd}(\text{F}_6\text{acac})_2(\text{bpy})$. In addition, we find that in solution, this compound undergoes an unusual exchange process involving the hexafluoroacetylacetonate (F_6acac) ligand. Detailed characterization of the $n = 2$ class is especially important since this type of material is formed as a surface compound when $\text{Pd}(\text{F}_6\text{acac})_2$ reacts with condensed-phase donors such as alumina.²

Synthetic Chemistry and Physical Properties

When $\text{Pd}(\text{F}_6\text{acac})_2$ in nonpolar solvents is treated with a Lewis base, the limiting composition, i.e., the highest value for n in $\text{Pd}(\text{F}_6\text{acac})_2\cdot n\text{L}$, appears to be thermodynamically

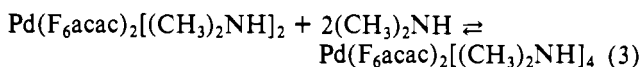
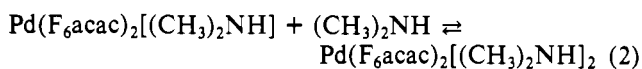
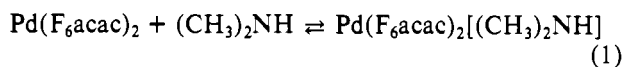
determined by a combination of the steric and electronic properties of the base. Thus, triphenylarsine, bis(diphenylarsino)methane, phenothiazine (PTZ), and phenoselenazine (PSZ) generate in isolable amounts only adducts of the $n = 2$ class, regardless of the amount of base employed. The effect of the electronic nature of the base is seen in a comparison of the products formed from triphenylphosphine and triphenylarsine in solvents of low dielectric constant such as chloroform or toluene. The former yields only the 1:1 adduct $\text{Pd}(\text{F}_6\text{acac})_2\cdot \text{Ph}_3\text{P}^3$ whereas the latter produces $\text{Pd}(\text{F}_6\text{acac})_2\cdot (\text{Ph}_3\text{As})_2$ (1). The effect of the steric properties of the donor is shown in a comparison of the chemistry of ammonia and the methylamines $(\text{CH}_3)_x\text{NH}_{3-x}$. Treatment of $\text{Pd}(\text{F}_6\text{acac})_2$ in pentane with excess trimethylamine affords $\text{Pd}(\text{F}_6\text{acac})_2\cdot [(\text{CH}_3)_3\text{N}]_2$ (3). Under the same conditions, the less sterically hindered donors ammonia and methylamine yield $\text{Pd}(\text{F}_6\text{acac})_2(\text{NH}_3)_4$ and $\text{Pd}(\text{F}_6\text{acac})_2(\text{CH}_3\text{NH}_2)_4$. The behavior of dimethylamine, with intermediate steric bulk, is different in that the equilibrium constants for the formation of the $n = 1, 2, 4$ adducts, eq 1-3, are sufficiently different that either

(1) A. R. Siedle and L. H. Pignolet, *Inorg. Chem.*, **20**, 1849 (1981).

(2) A. R. Siedle, P. M. Sperl, and T. W. Rusch, *Appl. Surf. Sci.*, **6**, 149 (1980).

(3) A. R. Siedle, L. H. Pignolet, and R. A. Newmark, to be submitted for publication.

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$\text{Pd}(\text{F}_6\text{acac})_2[(\text{CH}_3)_2\text{NH}]_2$ (**4**) or $\text{Pd}(\text{F}_6\text{acac})_2[(\text{CH}_3)_2\text{NH}]_4$ can be isolated in pure form by adjusting the amount of dimethylamine employed. When the amine:Pd ratio is $\leq 2:1$, a mixture of the 1:1 and 2:1 adducts is produced.¹

The equilibria represented by eq 2 and 3 are readily displaced. Thus, 2 mol of dimethylamine can be removed from $\text{Pd}(\text{F}_6\text{acac})_2[(\text{CH}_3)_2\text{NH}]_4$ by pumping under high vacuum to form **4**. In chloroform solution, however, ¹⁹F and ¹³C NMR spectroscopic analyses show that $\text{Pd}(\text{F}_6\text{acac})_2[(\text{CH}_3)_2\text{NH}]_2$ disproportionates into $\text{Pd}(\text{F}_6\text{acac})_2[(\text{CH}_3)_2\text{NH}]_4$ and $\text{Pd}(\text{F}_6\text{acac})_2$. One mole of trimethylamine is removed from **3** by prolonged pumping, converting it into $\text{Pd}(\text{F}_6\text{acac})_2(\text{CH}_3)_3\text{N}$. Similarly, recrystallization of $\text{Pd}(\text{F}_6\text{acac})_2(t\text{-C}_4\text{H}_9\text{NC})_4$ from hot hexane converts it into the 2:1 adduct $\text{Pd}(\text{F}_6\text{acac})_2(t\text{-C}_4\text{H}_9\text{NC})_2$ (**5**). In this case, the formation of **5** is assisted by a palladium-catalyzed polymerization of the liberated isocyanide. Ligand lability is also reflected in the electron-impact mass spectra of $\text{Pd}(\text{F}_6\text{acac})_2\text{L}_2$, which typically show ions due to L and $\text{Pd}(\text{F}_6\text{acac})_2$ but not the complex.

The 2:1 $\text{Pd}(\text{F}_6\text{acac})_2$ adducts are conveniently isolated from hydrocarbon solvents as yellow or orange crystalline materials. Analytical and spectroscopic data are collected in Tables S1–S4 (supplementary material). Infrared spectra of these compounds, both as Nujol mulls and in chloroform, all show strong bands at about 1670 cm^{-1} , due to the C=O group mode in the F_6acac units, and three additional strong bands at about 1260, 1190, and 1135 cm^{-1} . The carbonyl band in particular is significantly shifted from its value of 1603 cm^{-1} in pure $\text{Pd}(\text{F}_6\text{acac})_2$. The spectrum of the dimethylamine complex **4** contains a strong N–H stretching band at 3150 cm^{-1} . The *tert*-butyl isocyanide derivative **5** exhibits a C=N stretch at 2235 cm^{-1} . In chloroform, it appears to dissociate as evidenced by the two methyl peaks in the ¹H NMR spectrum at 1.55 (free isocyanide) and 1.83 ppm.

Treatment of $\text{Pd}(\text{F}_6\text{acac})_2$ with ≥ 1 equiv of 2,2'-bipyridyl produces yellow crystalline $\text{Pd}(\text{F}_6\text{acac})_2(\text{bpy})$ (**6**). The ¹H NMR spectrum in acetone contains peaks due to the bipyridyl protons at δ 8.96 (H3), 8.56 (H4, H6), and 8.03 (H5). Unambiguous assignment of these multiplets (cf. Table S-4, supplementary material) is possible because coupling constants between ortho protons in aromatic rings are 7–9 Hz except for the α - β coupling in pyridines, which is about 6 Hz. The chemical shifts in **6** are sensitive to both solvent and solute concentrations, for which reasons differences between our assignments and those for $[\text{Pt}(\text{bpy})_2](\text{NO}_3)_2$ are not unexpected.⁴

From $\text{Pd}(\text{F}_6\text{acac})_2$ and 2 equiv of phenothiazine or phenoselenazine are obtained deep blue $\text{Pd}(\text{F}_6\text{acac})_2(\text{PTZ})_2$ (**7**) and $\text{Pd}(\text{F}_6\text{acac})_2(\text{PSZ})_2$ (**8**). On being heated, these compounds decompose without melting, and their infrared spectra contain the strong 1670- cm^{-1} bands typical of $\text{Pd}(\text{F}_6\text{acac})_2$ complexes. Unlike the other compounds reported in this paper, they are intensely colored, but dilute solutions in acetone are rapidly bleached in air. The visible spectrum of **7** in Nujol contains two bands at 580 and 740 nm and that of **8** at 610 and 735 nm. These low-energy absorptions are attributed to ligand \rightarrow metal charge-transfer processes, since the ligands themselves are readily oxidized to stable cation radicals. In this respect,

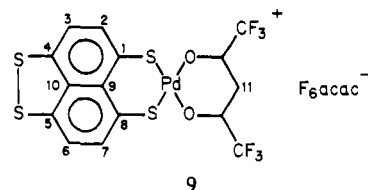
Table I. ¹³C NMR Data for (TTN) $\text{Pd}(\text{F}_6\text{acac})_2$

carbon position	shift, ppm	J_{CH} , Hz
1, 8	118.6	8
2, 7	132.6	168
3, 6	117.1	174
4, 5	152.0	9
9 or 10	135.5	0
11	83.5	158
CO	171.1	31 ^a
CF ₃	130.4	307 ^a

^a $^2J_{\text{CF}}$.

the optical spectra of **7** and **8** are similar to that of *trans*-(PTZ)₂PdCl₂⁴ and (TTF)₂PdCl₂⁵ (TTF = tetrathiafulvalene). The X-ray photoelectron (XPS) spectrum of **7** showed that the sulfur 2p_{1/2} core-level binding energy is 166.9 eV compared with 165.7 eV in pure phenothiazine. While the sulfur core levels are shifted by 1.2 eV, the respective nitrogen 1s levels are 400.4 and 400.6 eV. This strongly suggests that phenothiazine in **7** is bonded to palladium through sulfur. In agreement with this, we note that an X-ray crystal structure study of *cis*-(PSZ)₂PtCl₂·CH₃CN has shown that selenium is the donor atom.⁴

Another palladium-sulfur compound of the $\text{Pd}(\text{F}_6\text{acac})_2\text{L}_2$ class was prepared by the reaction of $\text{Pd}(\text{F}_6\text{acac})_2$ with tetrathianaphthacene (TTN), which led to (TTN) $\text{Pd}(\text{F}_6\text{acac})_2$ (**9**). Addition reactions of TTN with low-valent metal com-



pounds may be regarded as formal oxidative additions,^{6,7} but since the palladium in **9** remains in the +2 state, this formalism is probably not applicable here. Unlike many other metal complexes of TTN, **9** has sufficient solubility in organic solvents to use NMR spectroscopy as a structural probe. In Me₂SO-*d*₆, a singlet ¹⁹F resonance at δ 75.1 and a single peak at δ 6.08 in the ¹H spectrum due to the F_6acac groups are observed. The TTN ring protons exhibit an AX quartet with δ_A 7.74, δ_B 8.76, and $J_{\text{AX}} = 7$ Hz. This is indicative of addition of palladium across only one of the sulfur-sulfur bonds as shown in the proposed structure.

The protons with δ 7.74 are assigned to H3 on the basis of the greater similarity in chemical shift to those in TTN, δ 6.93 in acetone-CS₂. Further support for this structure was obtained from the ¹³C NMR spectrum summarized in Table I, which shows the expected asymmetry in the TTN ring. Assignment of C3 and C6 was made by comparison with the spectrum of pure TTN, which showed δ 118.3 for the aromatic protonated carbons. Only one quaternary ¹³C resonance at δ 135.5 was seen in the spectrum of **9**, and it could be due to either C9 or C10. Rapid exchange of the ionic and coordinated F_6acac groups, as demonstrated below for (bpy) $\text{Pd}(\text{F}_6\text{acac})_2$, appears to average the chemical shifts for these two groups. The X-ray photoelectron spectrum of **9** revealed that the Pd 3d_{5/2} binding energy was 338.3 eV (relative to C 1s at 285.0 eV), a value typical of Pd(II). The nonequivalent sulfur atoms were not resolved, and the S 2s core levels of both were 229.0 eV. The long-wavelength band in the electronic spectrum of

(5) M. C. Etter and A. R. Siedle, unpublished results.

(6) B. K. Teo, F. Wudl, J. J. Hauser, and A. Kruger, *J. Am. Chem. Soc.*, **99**, 2344 (1977).

(7) B. K. Teo, F. Wudl, J. J. Hauser, and A. Kruger, *J. Am. Chem. Soc.*, **99**, 4862 (1977).

(4) O. Farrer, O. Monsted, and G. Nord, *J. Am. Chem. Soc.*, **101**, 6118 (1979).

Table II. Selected Distances and Angles

Distances, Å							
Pd-N1	2.007 (7)	N1-C1	1.31 (1)	C6-C7	1.37 (1)	O3-C31	1.27 (1)
Pd-N2	1.966 (8)	N1-C5	1.38 (1)	C7-C8	1.42 (1)	O4-C33	1.23 (1)
Pd-O1	2.014 (6)	N2-C10	1.33 (1)	C8-C9	1.40 (1)	C31-C32	1.38 (2)
Pd-O2	1.996 (7)	N2-C6	1.37 (1)	C9-C10	1.38 (2)	C32-C33	1.37 (1)
Pd-O3	4.290 (7)	C5-C6	1.48 (1)	O1-C11	1.28 (1)	C31-C35	1.49 (2)
Pd-O4	3.479 (7)	C1-C2	1.38 (1)	O2-C13	1.26 (1)	C33-C34	1.57 (2)
Pd-Pd ^a	4.614 (3)	C2-C3	1.36 (1)	C11-C12	1.37 (1)	C35-F35 ^b	1.24 (2)
N1-N2	2.63 (1)	C3-C4	1.43 (2)	C12-C13	1.38 (1)	C34-C34 ^b	1.31 (2)
O1-O2	2.91 (1)	C4-C5	1.42 (2)	C11-C15	1.54 (2)	C15-F15 ^b	1.26 (2)
				C13-C14	1.55 (2)	C14-F14 ^b	1.29 (1)
Angles, Deg							
N1-Pd-N2	82.7 (3)	Pd-N2-C10	126.9 (7)	Pd-O1-C11	120.1 (6)		
O1-Pd-O2	92.9 (3)	Pd-N2-C6	115.3 (7)	Pd-O2-C13	123.1 (7)		
N1-Pd-O1	175.1 (3)	Pd-N1-C1	126.0 (7)	O1-C11-C12	133 (1)		
N1-Pd-O2	92.0 (3)	Pd-N1-C5	112.7 (7)	O2-C13-C12	130 (1)		
N2-Pd-O1	92.4 (3)	N2-C6-C5	113.8 (9)	C11-C12-C13	120 (1)		
N2-Pd-O2	174.7 (3)	N1-C5-C6	115.4 (9)				

^a Pd position generated by inversion operation. ^b Average C-F distance.

9, attributed to a ligand → metal charge-transfer process, shifts to lower energy with increasing solvent polarity and occurs at 503, 562, and 580 nm in toluene, acetonitrile, and dimethyl sulfoxide, respectively.

As confirmed by the diffraction study described below, the 2:1 adducts of Pd(F₆acac)₂ are salts in which one of the covalent F₆acac groups has been displaced by two adjacent ligands, and they may be formulated as [L₂Pd(O,O-F₆acac)]⁺F₆acac⁻, which contain an oxygen-bonded bidentate F₆acac ligand and an ionic F₆acac. In chloroform, it is likely that tight ion pairing occurs. The molecular weights, obtained by vapor-pressure osmometry, of Pd(F₆acac)₂(Ph₃As)₂ and Pd(F₆acac)₂(bpy) in this solvent were 713 and 621, respectively, compared with the values of 1114 and 676 calculated with the assumption of no ionization. Evidence for an ionic nature was obtained from conductivity measurements in nitromethane over a concentration range of 10⁻³–10⁻⁵ M. Plots of (Δ₀ - Δ_e) vs. c^{1/2} were linear with slopes of 208 and 160 for **1** and **6**, respectively, indicating that these compounds are 1:1 electrolytes.⁸ In accordance with this, one of the F₆acac groups may be removed by metathetical reactions. When methanol solutions of **1** or **6** were treated with ammonium hexafluorophosphate, [(Ph₃As)₂Pd(F₆acac)]PF₆ (**10**) and [(bpy)Pd(F₆acac)]PF₆ (**11**) were obtained in nearly quantitative yield. The ¹⁹F and ¹H spectra of these compounds contain sharp singlets at δ 73.8 and 6.6 (cf. Table S-4, supplementary material).

The ¹⁹F and ¹H NMR spectra of the Pd(F₆acac)₂L₂ compounds exhibit broad singlets for the F₆acac moieties. Since one would expect separate resonances for coordinated and ionic F₆acac, this suggests that there is an exchange between these two groups that is rapid on the NMR time scale. The 2,2'-bipyridyl derivative [(bpy)Pd(F₆acac)]F₆acac (**6**) was chosen for further study since it was stable in solution, and the chelating nature of the bpy ligand should ensure that its dissociation would not contribute to the complexity of variable-temperature NMR spectra. The ¹⁹F NMR spectrum of **6** at 24 °C shows a very broad peak (240-Hz width at half-height) at 74.71 ppm in acetonitrile solvent. When the solution is cooled to -21 °C, two sharp singlets emerge, separated by 258 Hz, at 72.95 and 75.69 ppm. These are assigned to coordinated and ionic F₆acac, respectively. Both peaks are shifted upfield by 0.01 ppm/deg, but fitting of the data at low temperatures where a doublet is observed indicates that the chemical shift difference between fluorines in these two environments is independent of temperature. Spectra obtained

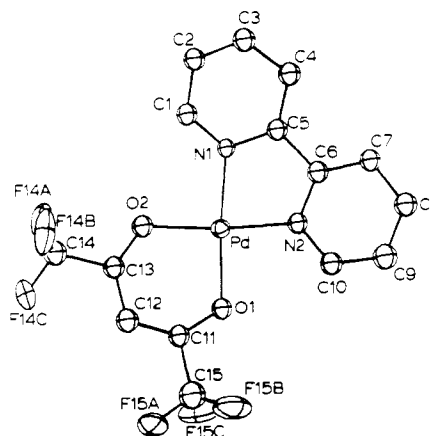


Figure 1. ORTEP drawing of [(bpy)Pd(F₆acac)]⁺. The thermal ellipsoids are drawn with 30% probability boundaries.

over the temperature range -21 to +72 °C showed a classical dynamic equilibrium from fluorine exchange in two equally populated sites.⁹ Free energies of interconversion were calculated at seven temperatures with use of the equations of Gutowsky and Holm¹⁰ and are given in Table S-5 (supplementary material) along with lifetimes and line widths. A least-squares fit to ΔG = ΔH - T(ΔS) yields ΔH[‡] = 10.4 ± 1 kcal/mol and ΔS[‡] = -11 ± 4 eu for the F₆acac exchange.

The mechanistic details of the exchange between ionic and bidentate oxygen-bonded F₆acac remain to be elucidated. Such an interconversion is uncommon for η₂-diketonates, but some related reactions have been reported. These include exchange in asymmetric platinum and palladium chelates,¹¹ exchange of acetylacetonate between Ph₂Sn(acac)₂ and (CH₃)₂Sn(acac)₂,¹² and an unusual metal exchange between Cu(F₆acac)₂ and [N,N'-ethylenebis(salicylideneiminato)]cobalt(II).¹³ In order to further characterize solid (bpy)Pd(F₆acac)₂, we carried out a single-crystal X-ray structure determination.

Description of the Structure

The crystal structure of (bpy)Pd(F₆acac)₂ consists of [(bpy)Pd(F₆acac)]⁺ cation and F₆acac⁻ anion units weakly

- (9) R. J. Abraham and P. Loftus, "Proton and Carbon-13 NMR Spectroscopy", Heyden, London, 1978.
 (10) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956). Values of τ cited in Table S-5 (supplementary material) are equal to τ_A in this reference, corresponding to current usage.
 (11) C. J. May and J. Powell, *Inorg. Chim. Acta*, **26**, L21 (1978).
 (12) N. Serpone and R. Ishayek, *Inorg. Chem.*, **13**, 52 (1974).
 (13) N. B. O'Bryan, T. O. Maier, I. C. Paul, and R. S. Drago, *J. Am. Chem. Soc.*, **95**, 6640 (1973).

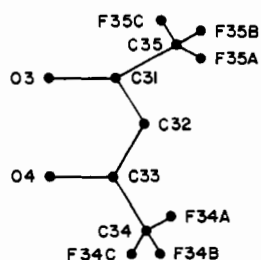
(8) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1972).

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
Pd	0.15873 (8)	0.0618 (1)	0.07598 (5)	2.93 (3)	3.70 (4)	3.00 (4)	0.15 (6)	0.68 (3)	-0.18 (7)
F14A	0.1327 (8)	-0.316 (1)	0.2152 (5)	9.1 (6)	9.3 (6)	9.4 (6)	-3.7 (5)	0.1 (5)	4.5 (5)
F14B	0.2030 (11)	-0.156 (1)	0.2806 (5)	21.3 (9)	5.3 (5)	5.8 (5)	0.6 (6)	6.2 (5)	0.7 (5)
F14C	0.3027 (8)	-0.321 (1)	0.2567 (5)	7.9 (5)	10.5 (6)	9.6 (6)	2.3 (5)	1.4 (5)	6.4 (5)
F15A	0.5736 (7)	-0.125 (2)	0.1525 (5)	3.3 (4)	26 (1)	9.6 (6)	2.2 (6)	0.0 (4)	9.0 (7)
F15B	0.5427 (7)	0.048 (1)	0.0892 (7)	4.5 (4)	8.1 (6)	27 (1)	0.1 (5)	4.4 (6)	5.0 (8)
F15C	0.5086 (8)	-0.153 (2)	0.0592 (6)	6.5 (4)	17 (1)	13.8 (7)	1.8 (6)	5.6 (4)	-2.6 (8)
F34A	0.2550 (8)	-0.173 (1)	0.2692 (5)	8.7 (6)	9.6 (7)	8.5 (6)	0.1 (6)	1.3 (5)	2.3 (6)
F34B	0.1589 (11)	0.348 (1)	0.2885 (5)	18.8 (9)	7.5 (6)	5.7 (5)	-0.4 (7)	4.4 (5)	-3.1 (5)
F34C	0.0812 (8)	0.170 (1)	0.2342 (5)	8.5 (5)	10.0 (7)	8.1 (6)	-2.2 (5)	1.9 (5)	0.5 (6)
F35A	0.5131 (9)	0.337 (2)	0.1505 (8)	7.1 (6)	20 (1)	26 (1)	3.9 (8)	5.3 (7)	9 (1)
F35B	0.4963 (11)	0.541 (2)	0.1450 (10)	9.5 (7)	12.5 (8)	44 (2)	-3.3 (7)	8.8 (9)	-1 (1)
F35C	0.4684 (11)	0.419 (3)	0.0662 (7)	9.4 (7)	54 (3)	13.0 (8)	1 (1)	6.0 (6)	-1 (2)

atom	x	y	z	B ₁₁	atom	x	y	z	B ₁₁
O1	0.3230 (7)	0.0216 (9)	0.0739 (4)	3.8 (2)	C8	0.104 (1)	0.408 (2)	-0.0928 (7)	4.6 (3)
O2	0.1568 (6)	-0.0791 (9)	0.1472 (4)	3.9 (2)	C9	0.211 (1)	0.347 (2)	-0.0733 (7)	5.4 (4)
O3	0.2622 (9)	0.5041 (13)	0.0816 (6)	7.7 (3)	C10	0.228 (1)	0.246 (1)	-0.0240 (7)	4.3 (3)
O4	0.0935 (9)	0.3794 (11)	0.1481 (5)	6.5 (3)	C11	0.382 (1)	-0.061 (2)	0.1165 (6)	3.9 (3)
N1	-0.0055 (8)	0.112 (1)	0.0711 (5)	2.9 (2)	C12	0.355 (1)	-0.141 (2)	0.1660 (7)	4.4 (3)
N2	0.1459 (8)	0.204 (1)	0.0060 (5)	3.4 (2)	C13	0.245 (1)	-0.142 (1)	0.1771 (6)	3.9 (3)
C1	-0.073 (1)	0.057 (2)	0.1068 (6)	3.8 (3)	C14	0.219 (1)	-0.234 (2)	0.2338 (7)	5.1 (4)
C2	-0.184 (1)	0.102 (1)	0.1015 (6)	3.9 (3)	C15	0.505 (1)	-0.064 (2)	0.1065 (7)	6.4 (4)
C3	-0.223 (1)	0.206 (2)	0.0579 (7)	4.4 (3)	C31	0.325 (1)	0.428 (2)	0.1245 (7)	5.9 (4)
C4	-0.157 (1)	0.266 (1)	0.0146 (7)	4.3 (3)	C32	-0.294 (1)	0.658 (2)	-0.1715 (7)	4.8 (3)
C5	-0.044 (1)	0.214 (1)	0.0243 (6)	3.7 (3)	C33	0.184 (1)	0.336 (2)	0.1804 (7)	4.6 (3)
C6	0.041 (1)	0.265 (1)	-0.0128 (7)	3.8 (3)	C34	0.164 (1)	0.261 (2)	0.2436 (8)	6.2 (4)
C7	0.015 (1)	0.367 (1)	-0.0604 (6)	3.9 (3)	C35	0.447 (2)	0.432 (2)	0.1189 (9)	8.6 (5)

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

Figure 2. Labeling scheme for the noncoordinated F₆acac anion.

linked by a short oxygen-hydrogen interaction (O3...H4 = 1.97 Å). H4 is the hydrogen atom bonded to C4 of the bipyridyl ring, and its position was calculated by assuming a C-H

distance of 1.08 Å, and O3 is an oxygen atom in the F₆acac anion. An ORTEP drawing of the cation is shown in Figure 1, and the labeling scheme for the anionic F₆acac unit is shown in Figure 2. An ORTEP stereoview of the contents of one unit cell is shown in Figure 3. Selected distances and angles are presented in Table II.

The coordination geometry around the palladium atom is approximately square planar. The Pd atom is only 0.006 (1) Å out of the weighted least-squares plane formed by N1, N2, O1, and O2 (Table S-6, supplementary material). The major distortion from idealized square-planar geometry is caused by the non-90° bite angles of the five- and six-membered chelate rings formed by the bpy and F₆acac ligands, respectively. These chelate bite angles compare well with the values observed in [(bpy)₂Pd](NO₃)₂·H₂O¹⁴ (79.9 and 80.1°) and in

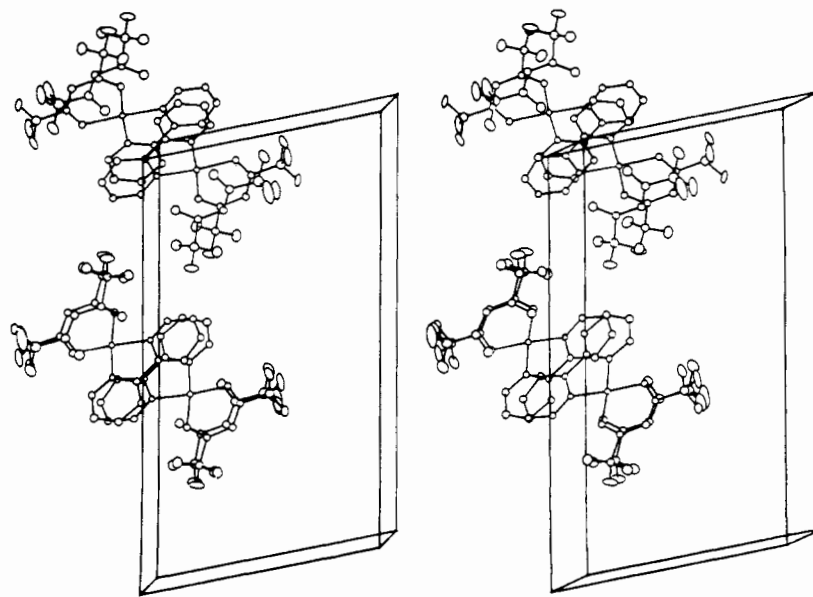


Figure 3. ORTEP stereoview of the contents of one unit cell showing the packing.

$[(\text{CH}_3)_2\text{NH}]\text{Pd}(\text{F}_6\text{acac})_2$ (92.5°).¹ The Pd-N distances are the same within 5 esd's (Pd-N1 = 2.007 (7) Å and Pd-N2 = 1.966 (8) Å) and are slightly shorter than the distances found in $[(\text{bpy})_2\text{Pd}](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ (average 2.034 (1) Å). Both Pd-O distances are the same within 1 esd (Pd-O1 = 2.014 (6) Å and Pd-O2 = 1.996 (7) Å) and are similar to the values found in $[(\text{CH}_3)_2\text{NH}]\text{Pd}(\text{F}_6\text{acac})_2$ (average Pd-O = 2.03 Å).

The bipyridyl and chelated F_6acac ligands are each planar within experimental error (Table S-6, supplementary material), and the dihedral angle between their least-squares planes is only 5.7°. The dihedral angles between the N1, N2, O1, and O2 coordination plane and the planes formed by the bpy and F_6acac groups are 0.2 and 5.5°, respectively. Therefore, the entire cationic $(\text{bpy})\text{Pd}(\text{F}_6\text{acac})^+$ unit is essentially planar except for the fluorine atoms. This is especially evident in the ORTEP stereoview, Figure 3. The anionic F_6acac^- unit is slightly twisted from a planar geometry. The molecules pack in such a way that the planar $(\text{bpy})\text{Pd}(\text{F}_6\text{acac})^+$ units, which are related by an inversion center, are parallel with the usual slipped-stack geometry for the bipyridyl rings (cf. Figure 3).¹⁵ The closest contact between these rings is 3.39 Å for N2...C1.

The distances within the F_6acac ligand are normal. Within the chelated F_6acac ligand, the C13-O2 and C11-O1 distances are identical within experimental error as are those between C12-C13 and C11-C12, indicating that the chelate ring is symmetrical. There is no evidence for unsymmetrical bonding as found in $[(\text{CH}_3)_2\text{NH}]\text{Pd}(\text{F}_6\text{acac})_2$ and in the bis(pyridine) adducts of $\text{Zn}(\text{F}_6\text{acac})_2$ and $\text{Cu}(\text{F}_6\text{acac})_2$.¹⁶ Bond distances within the bipyridyl ligand also appear normal.¹⁷ However, the C5-N1 and C6-N2 distances, the atoms of which form part of the Pd-N1-C5-C6-N2 five-membered ring, are 1.38 (1) and 1.37 (1) Å, respectively. These are significantly longer than the C1-N1 and C10-N2 distances, respectively, 1.31 and 1.33 (1) Å. An opposite effect has been noted in *trans*- $[\text{Ru}(\text{bpy})_2(\text{OH}_2)(\text{OH})]\text{ClO}_4$ ¹⁸ in whose structure the standard deviations were much smaller.

Experimental Section

Infrared spectra were obtained on Nujol mulls with use of a spectrometer with grating optics and are believed to be accurate to within $\pm 5 \text{ cm}^{-1}$.

Palladium Bis(hexafluoroacetylacetonate). An aqueous solution of sodium hexafluoroacetylacetonate was prepared by stirring 4.15 g (20 mmol) of hexafluoroacetylacetonate with 20 mL of 1 N sodium hydroxide until the diketone went into solution. To this was added 2.94 g (10 mmol) of Na_2PdCl_4 in 15 mL of water. After 1 h of stirring, the crude $\text{Pd}(\text{F}_6\text{acac})_2$ was collected on a filter, washed with water, and dried over calcium chloride. The product was dissolved in a minimum amount of hot hexane. Cooling the filtered solution to -78 °C afforded yellow $\text{Pd}(\text{F}_6\text{acac})_2$, which was further purified by vacuum sublimation. The yield was 2.2 g (42%). Anal. Calcd: C, 23.1; H, 0.4; F, 43.9; Pd, 20.4. Found: C, 23.0; H, 0.5; F, 43.8; Pd, 20.7.

$(\text{Ph}_3\text{As})_2\text{Pd}(\text{F}_6\text{acac})_2$ (1). A 0.61-g (2-mmol) quantity of triphenylarsine (recrystallized from ethanol) and 0.52 g (1 mmol) of $\text{Pd}(\text{F}_6\text{acac})_2$ were stirred together with 15 mL of toluene. The red solution was diluted with 50 mL of hexane. After the solution stood for 4 h, the deep red crystals were collected on a filter, washed with hexane, and vacuum-dried. The yield was 0.89 g (79%).

$[(\text{CH}_3)_3\text{N}]_2\text{Pd}(\text{F}_6\text{acac})_2$ (3). A stream of dry trimethylamine was passed into a solution of 0.52 g of $\text{Pd}(\text{F}_6\text{acac})_2$ in 10 mL of pentane. The reaction mixture darkened and then turned light orange as yellow crystals began to separate. After 5 min, the reaction mixture was filtered to give 0.5 g of 3, which was dried under stream of nitrogen. This compound was converted to $\text{Pd}(\text{F}_6\text{acac})_2 \cdot (\text{CH}_3)_3\text{N}$ by pumping for 4 h at a nominal pressure of 5×10^{-6} mm. Anal. Calcd: C, 26.9;

H, 1.9; N, 2.4. Found: C, 26.5; H, 1.9; N, 2.4.

$\text{Pd}(\text{F}_6\text{acac})_2(t\text{-C}_4\text{H}_9\text{NC})_4$ and $\text{Pd}(\text{F}_6\text{acac})_2(t\text{-C}_4\text{H}_9\text{NC})_2$ (5). A solution of 0.50 g (6 mmol) of *tert*-butyl isocyanide in 5 mL of pentane was added to 0.52 g of $\text{Pd}(\text{F}_6\text{acac})_2$ in 15 mL of the same solvent. White $\text{Pd}(\text{F}_6\text{acac})_2(t\text{-C}_4\text{H}_9\text{NC})_4$ separated and was isolated by filtration. After the solid was dried in a stream of nitrogen, the yield was 0.68 g (80%).

A 0.5-g sample of this adduct was treated with 15 mL of boiling hexane. After filtration to remove oily material, the hexane extract was cooled to -20 °C to afford 0.17 g (42%) of 5 as cream-colored crystals.

$\text{Pd}(\text{F}_6\text{acac})_2\text{-bpy}$ (6). A solution of 0.26 g of $\text{Pd}(\text{F}_6\text{acac})_2$ in 8 mL of toluene was added to 0.08 g (0.5 mmol) of 2,2'-bipyridyl in 3 mL of toluene. The product separated as small yellow crystals, which were collected on a filter, washed with toluene, and vacuum-dried. The yield was 0.32 g (95%). Crystals of 6 used for the X-ray structure determination were grown by slow evaporation of a dichloromethane solution.

$\text{Pd}(\text{F}_6\text{acac})_2(\text{PTZ})_2$ (7). Commercial phenothiazine was purified by three recrystallizations from ethanol followed by vacuum sublimation. Phenothiazine, 0.20 g (1.0 mmol), and 0.26 g of $\text{Pd}(\text{F}_6\text{acac})_2$ were combined in 20 mL of acetone. Toluene, 3 mL, was added, and the resulting solution was concentrated under reduced pressure to give 0.38 g of 7 as deep blue microcrystals. X-ray powder pattern [d , Å (I/I_0): 12.54 (15), 10.83 (100), 8.01 (30), 7.57 (80), 6.78 (20), 5.76 (20), 4.41 (50), 4.01 (15)]. The preparation of $\text{Pd}(\text{F}_6\text{acac})_2(\text{PSZ})_2$ (8) was carried out in a similar manner. X-ray powder pattern: 12.99 (30), 10.93 (100), 7.57 (60), 6.66 (15), 6.18 (20).

$[(\text{Pb}_3\text{As})_2\text{Pd}(\text{F}_6\text{acac})]\text{PF}_6$ (10). Triphenylarsine, 1.22 g (4 mmol), and 1.08 g (2 mmol) of $\text{Pd}(\text{F}_6\text{acac})_2$ were combined in 75 mL of methanol. The reaction mixture was stirred until the arsine dissolved, treated with 8 mmol of NH_4PF_6 in methanol, and diluted to the cloud point with water. Methanol was slowly removed under reduced pressure on a rotary evaporator until the separation of small yellow crystals was complete. These were collected on a filter, washed with water and then diethyl ether, and vacuum-dried. The yield was 2.0 g (93%).

$(\text{TTN})\text{Pd}(\text{F}_6\text{acac})_2$ (9). A mixture of 0.52 g (1 mmol) of $\text{Pd}(\text{F}_6\text{acac})_2$ and 0.13 g (0.5 mmol) of tetrathianaphthacene in 50 mL of benzene was placed in a flask fitted with a calcium chloride drying tube. This was refluxed for 16 h, cooled to room temperature, filtered, and diluted with methylcyclohexane. Slow evaporation of the benzene afforded 0.30 g of 9 as dark purple crystals. They were extracted overnight with pentane in a Soxhlet apparatus to remove traces of soluble impurities. Cyclic voltammetry in acetonitrile showed no reversible electrochemical processes. Conductivity measurements, made on compressed pellets of the compound, showed that it is an insulator.

The NMR spectra were obtained on a Varian XL-100 spectrometer at 100 MHz (¹H) or 94.2 MHz (¹⁹F). Variable-temperature spectra of $(\text{bpy})\text{Pd}(\text{F}_6\text{acac})_2$ were obtained in CH_3CN (CFCl_3 reference). Temperatures were determined by substituting a tube of neat ethylene glycol or methanol for the analytical sample before or after each NMR spectrum. The temperatures were then determined from the calibration charts of Van Geet and Kaplan et al.¹⁹⁻²¹ The accuracy of these data has recently been confirmed by Becker et al.²² The signal in the neat "temperature reference" samples was sufficient that the necessary proton spectra could be obtained without retuning the preamp or transmitter coils on the XL-100. The line width in the absence of exchange, taken as that of the reference CFCl_3 or solvent CH_3CN , under 2 Hz in all spectra, was subtracted from the observed line width to give the exchange broadening. This correction was not a significant factor due to the broad lines observable over a 90 deg wide temperature range. Lifetimes (τ) of the two types of F_6acac were determined by calculating spectra with the equations of Gutowsky and Holm as a function of τ on a Hewlett-Packard 67 calculator.¹⁰ Free energies of activation were calculated from absolute reaction rate theory.

The major dependence of the experimental temperature in the calculation of ΔH^\ddagger and ΔS^\ddagger is in ΔG^\ddagger . Maximum errors in ΔH and

(14) P. C. Chieh, *J. Chem. Soc., Dalton Trans.*, 1643 (1972).

(15) F. Herbstein in "Perspectives in Structural Chemistry", Vol. 4, J. D. Dunitz and J. A. Ibers, Eds., Wiley, New York, 1971, p 166.

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

(17) E. D. McKenzie, *Coord. Chem. Rev.*, **6**, 187 (1971).

(18) B. Durham, S. R. Wilson, D. J. Hodgson, and T. J. Meyer, *J. Am. Chem. Soc.*, **102**, 600 (1980).

(19) A. L. Van Geet, *Anal. Chem.*, **40**, 2227 (1968).

(20) A. L. Van Geet, *Anal. Chem.*, **42**, 679 (1970).

(21) M. L. Kaplan, F. A. Bovey, and H. N. Cheng, *Anal. Chem.*, **47**, 1703 (1975).

(22) D. S. Raiford, C. L. Fisk, and E. D. Becker, *Anal. Chem.*, **51**, 2050 (1979).

ΔS were calculated by assuming the worse possible systematic errors of $\pm 3^\circ\text{C}$ in the lower temperatures and $\pm 3^\circ\text{C}$ in the upper ones. The ΔG^\ddagger values were recalculated, and maximum errors of ± 0.8 for ΔH^\ddagger and ± 3 for ΔS^\ddagger were found compared to the values reported above. These errors are small compared to most thermodynamic parameters determined from dynamic NMR studies because the large chemical shift, 258 Hz, results in spectra that are a function of the dynamic equilibrium over a 90°C range.

Structure Determination. A small crystal of (bpy)Pd(F₆acac)₂ (**6**), PdF₁₂N₂O₄C₂₀H₁₀ ($M_r = 676.7$), of dimensions $0.20 \times 0.15 \times 0.10$ mm was selected and used in the structure determination. This crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD-4SDP automatic peak searching, centering, and indexing computer programs.²³ The space group $P2_1/c$ was chosen by the systematic absences during data collection and was verified by successful solution and refinement (vide infra). The unit cell parameters were determined by least-squares refinement of the angular settings of 25 Mo K α ($\lambda = 0.71069 \text{ \AA}$) peaks centered on the diffractometer at ambient temperature and are $a = 11.991(5) \text{ \AA}$, $b = 9.295(4) \text{ \AA}$, $c = 21.008(9) \text{ \AA}$, $\beta = 101.32(2)^\circ$, and $V = 2305 \text{ \AA}^3$. The density is calculated to be 1.950 g/cm^3 on the assumption of $Z = 4$. A total of 2815 unique reflections were measured in the scan range $2\theta = 0\text{--}44^\circ$ over one quadrant ($+h, +k, \pm l$) with use of graphite-monochromatized Mo K α radiation and a variable-rate $\omega\text{--}2\theta$ scan technique. No decay was noted in the intensity of three check reflections measured at intervals of 200 sequential reflections. Background counts were measured at both ends of the scan range with the 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. After correction for Lorentz, polarization, and background effects (but not for absorption; $\mu = 9.34 \text{ cm}^{-1}$),²⁴ 1526

reflections were judged observed [$F_o^2 \geq 2.5\sigma(F_o^2)$] and were used in all subsequent calculations.

Conventional heavy-atom techniques were used to solve the structure, and refinement with the palladium and fluorine atoms thermally anisotropic and all other nonhydrogen atoms thermally isotropic by full-matrix least-squares methods (222 variables) led to convergence of R and R_w at their final values of 0.057 and 0.063, respectively.²⁵ The error in an observation of unit weight was determined to be 1.78 by using a value of 0.06 for p in the $\sigma(I)$ equation.²⁴ The final difference Fourier map did not reveal any chemically significant features.

The final atomic coordinates with their estimated standard deviations and the final thermal parameters are given in Table III. Tables of observed and calculated structure factor amplitudes are available as supplementary material. Figure 1 presents an ORTEP perspective of the molecular structure of the (bpy)Pd(F₆acac)⁺ ion and shows the labeling scheme. The labeling scheme for the F₆acac⁻ anion is shown in Figure 2.

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Registry No. **1**, 78128-23-1; **2**, 78128-25-3; **3**, 78128-27-5; **4**, 78128-28-6; **5**, 78128-30-0; **6**, 65353-89-1; **7**, 78128-32-2; **8**, 78128-34-4; **9**, 78128-36-6; **10**, 78128-37-7; **11**, 78128-38-8; Pd(F₆acac)₂(*t*-C₄H₉NC)₄, 78149-17-4; Pd(F₆acac)₂, 64916-48-9.

Supplementary Material Available: Tables of analytical data and melting points (Table S-1), infrared data (Table S-2), electronic spectral data (Table S-3), NMR data (Table S-4), free energy data (Table S-5), weighted least-squares planes (Table S-6), and observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

(23) All calculations were carried out on PDP8A and 11/34 computers with use of the Enraf-Nonius CAD 4SDP programs. This crystallographic computing package is described in the following references: B. A. Frenz in "Computing in Crystallography", H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G. C. Bassi, Eds, Delft University Press, Delft, Holland, 1978, pp 64-71; "CAD4SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978.

(24) The intensity data were processed as described in "CAD4SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity $I = (K/NPI)(C - 2B)$, where $K = 20.1166 \times$ (attenuator factor), $NPI =$ ratio of fastest possible scan rate to the 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 $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$.

(25) 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 follows: $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$ 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 $[\sum w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$, where NO and NV are the number of observations and variables, respectively. Atomic scattering factors were taken from "International Tables for X-ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962. Anomalous dispersion corrections from the same source were used for palladium.