

pseudo-first-order conditions with excess reductant ($[Cl^-] = 0.94 \text{ M}$). The perchlorate salt ($[Co_2]_t = 5 \times 10^{-4} \text{ M}$) was dissolved in water and was mixed with solutions containing hydrogen ions ($[H^+] = 0.1-0.9 \text{ M}$), chromous ions ($[Cr(II)] = 0.02-0.04 \text{ M}$), and chloride ions. The reaction products were $[(H_2O)_5CrCl]^{2+}$, $[Co(OH_2)_6]^{2+}$, and the free ligand $Me_3[9]\text{-aneN}_3$ in its protonated form. Kinetic data are given in Table V. The rate law (eq 2) is independent of $[H^+]$ and first order

$$k_{\text{obsd}} = k_{Cr}[Cr^{2+}] \quad (2)$$

in $[Cr^{2+}]$ at constant $[Cl^-]$. This is taken as further evidence that no bridge-cleavage processes occur in acidic solution. The cation $[(Me_3[9]\text{-aneN}_3)_2Co_2(OH)_3]^{3+}$ is reduced by the strong reductant $[(H_2O)_5CrCl]^+$ via an outer-sphere process. It is noted that there is no experimental evidence for the reduction of a protonated species as has been proposed in ref 28.

In contrast to the simple rate law eq 2 a considerably more complex expression is found for the reduction of the $[(9]\text{-aneN}_3)_2Co_2(OH)_3]^{3+}$ cation by $[Cr(OH_2)_6]^{2+}$ in the $[H^+]$ range 0.05-0.3 M (eq 3). The details of this work will be

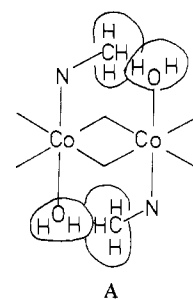
$$k_{\text{obsd}} = a + b[H^+] + c[H^+][Cr(II)] \quad (3)$$

described elsewhere.³⁰ It is not obvious why the equilibrium eq 1 is shifted completely to the left-hand side when 1,4,7-trimethyl-1,4,7-triazacyclononane is the ligand L and why a value of $K = 11 \pm 2 \text{ M}^{-1}$ (20 °C, $\mu = 1.0 \text{ M}$) is found for the analogous complex with the nonmethylated ligand 1,4,7-triazacyclononane.⁶

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(31) Thewalt, U. Z. *Anorg. Allg. Chem.* 1975, 412, 29.

From space-filling models (structure A) it can be shown that



with $Me_3[9]\text{-aneN}_3$ being the ligand the product, a diaqua-bis(μ -hydroxo) species cannot be formed because a sterically demanding CH_3 group of each ligand will interfere with the steric demands of the respective aqua ligand. The same explanation may account for the unreactivity of the corresponding complexes of chromium(III) and of rhodium(III) toward acid-catalyzed OH-bridge cleavage.

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Registry No. $[Cr_2(Me_3[9]\text{-aneN}_3)_2(OH)_3]I_3 \cdot 3H_2O$, 81898-05-7; $Cr(Me_3[9]\text{-aneN}_3)Cl_3$, 81915-50-6; $[Cr_2(Me_3[9]\text{-aneN}_3)_2(OH)_3](ClO_4)_3$, 81915-52-8; $[Co_2(Me_3[9]\text{-aneN}_3)_2(OH)_3](ClO_4)_3$, 81898-07-9; $[Rh_2(Me_3[9]\text{-aneN}_3)_2(OH)_3](ClO_4)_3$, 81898-09-1; $[Rh_2(Me_3[9]\text{-aneN}_3)_2(OH)_3]I_3$, 81898-10-4.

Supplementary Material Available: Listings of observed and calculated structure factors and anisotropic thermal parameters for $[(Me_3[9]\text{-aneN}_3)_2Cr_2(OH)_3]I_3 \cdot 3H_2O$ (10 pages). Ordering information is given on any current masthead page.

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Structure and Properties of a Palladium Methoxide Derivative, $Pd_2(\mu-CH_3O)_2(F_6acac)_2$. Reactions of Palladium Bis(hexafluoroacetylacetonate) with Aliphatic Alcohols

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Palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, reacts with methanol at room temperature to produce $Pd_2(\mu-CH_3O)_2(F_6acac)_2$. Crystal data: $P2_1/c$; $a = 8.945$ (4), $b = 7.149$ (6), $c = 29.36$ (1) Å; $\beta = 93.89$ (3)°; $V = 1873$ Å³; $Z = 4$. The molecule is a dimer with two methoxy groups bridging two nearly planar palladium atoms which are also attached to two η^2 - F_6acac ligands. The Pd_2O_2 ring is folded along the vector passing through the bridging oxygen atoms so that the dihedral angle between the PdO_2 planes is 26°. In the ring, $d(Pd-O)_{av}$ is 1.996 (7) Å and $d(Pd-Pd)$ is 2.984 (1) Å. At ca. 100 °C, the palladium methoxide decomposes to palladium metal, $Pd(F_6acac)_2$, methanol, methyl formate, and dimethoxymethane. $Pd(F_6acac)_2$ and 1-propanol react in the presence of oxygen to form propyl propionate, propionaldehyde, and propyl trifluoroacetate. The complex $[(C_3O_5)_2Pd]^{2-}$ was prepared from croconate(2-) and $Pd(F_6acac)_2$.

Introduction

The electron-withdrawing effect of the four trifluoromethyl groups in palladium bis(hexafluoroacetylacetonate), $Pd(F_6acac)_2$, leads to strong metal-centered acceptor behavior in this fluorinated organometallic compound. Facile displacement of chelating and oxygen- and carbon-bonded F_6acac groups is the source of an extensive acid-base chemistry as illustrated by our previous characterization of 1:1, 2:1, 3:1, and 4:1 adducts of $Pd(F_6acac)_2$ with molecular Lewis basis¹⁻⁴ and 2:1 adducts with solid donors such as silica and alumina.^{5,6}

Since the hexafluoroacetylacetonate anion is a good leaving group, $Pd(F_6acac)_2$ is a useful reagent in cyclometallation⁷ and β -diketonate exchange reactions⁸ and in the synthesis of highly colored (η^2 -formazanyl)palladium compounds.⁹ The present paper extends the synthetic chemistry of $Pd(F_6acac)_2$ and

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describes the preparation, structure, and reactivity of a novel palladium alkoxide, Pd₂(μ-CH₃O)₂(F₆acac)₂, and the reaction of Pd(F₆acac)₂ with simple aliphatic alcohols.

Results and Discussion

Synthesis and Spectroscopic Properties of Pd₂(μ-CH₃O)₂(F₆acac)₂. Attempts to effect displacement of F₆acac⁻ from Pd(F₆acac)₂ by methoxide salts in a variety of solvents led to the decomposition of the starting material and the formation of palladium metal. However, solutions of Pd(F₆acac)₂ in methanol deposited, upon standing at room temperature, rust-colored crystals of Pd₂(μ-CH₃O)₂(F₆acac)₂ (1). A similar reaction employing CD₃OD was used to prepare Pd₂(μ-CD₃O)₂(F₆acac)₂ (2). The yield, based on Pd(F₆acac)₂ consumed, is 71%, but the conversion is only 40%. Efforts to increase the conversion by increasing the reaction time or temperature resulted in the formation of metallic palladium as a byproduct. Solid 1 may be stored for at least several months at -20 °C but gradually decomposes at room temperature. Differential scanning calorimetry revealed a rapid and complete decomposition (vide infra) beginning at 93 °C. 1 is insoluble in methanol or acetone, and dimethyl sulfoxide solutions were unstable. The most useful solvent found was carbon tetrachloride.

Characterization of the new palladium methoxide compounds was achieved by elemental analyses and by vibrational spectroscopy. The infrared spectrum of 1 showed strong bands at 1610, 1600, 1270, 1230, and 1160 cm⁻¹ due to the hexafluoroacetylacetonate ligand. A medium intensity band at 1010 cm⁻¹, assigned to the C-O stretching in the μ-CH₃O group, shifts to 985 cm⁻¹ in 2 due to the increased reduced mass of the bridging group. A 1430-cm⁻¹ absorption is attributed to a symmetrical methyl deformation mode, but is 2, this band is obscured by strong CF₃ peaks. Bands at 2830 and 2490 cm⁻¹ may be assigned to symmetric and asymmetric methyl C-H stretching modes, respectively. These shift to 2070 and 2320 cm⁻¹ in 2, but the shift in ν_s is about 100 cm⁻¹ smaller than expected. The hexafluoroacetylacetonate ν_{C-H} occurs at 3140 cm⁻¹ in 1 and at 3200 cm⁻¹ in 2. Overall, the effect on the infrared spectra of replacing μ-CH₃O by μ-CD₃O in Pd₂(μ-CH₃O)₂(F₆acac)₂ parallel that seen in the gas-phase spectra of alcohols and in high-resolution energy loss spectra of CH₃O groups on Cu(100).¹⁰

The ¹H NMR spectrum of Pd₂(μ-CH₃O)₂(F₆acac)₂ in carbon tetrachloride contained two singlets at δ 2.41 and 6.14 in a 3:1 ratio due respectively to the CH₃O and F₆acac groups. The 6.14 ppm resonance is also observed in 2, indicating that deuterium exchange between CD₃OD and the F₆acac proton has not occurred to a significant extent, a point of importance in our subsequent pyrolysis studies. The ¹⁹F NMR spectrum comprised a sharp singlet at 75.0 ppm. The NMR data establish that 1 is a symmetrical aggregate, [Pd(OCH₃)(F₆acac)]_n with n ≥ 2, since the compound corresponding to n = 1 would be coordinatively unsaturated. Osmometric and mass spectroscopic molecular weight determinations were inconclusive due to thermal instability but were suggestive of a dimer. So that the palladium alkoxide could be more thoroughly characterized, a single-crystal X-ray structure determination was carried out.

Description of the Structure. Crystalline Pd₂(μ-CH₃O)₂(F₆acac)₂ consists of discrete molecular units. The shortest intermolecular contact is between fluorine atoms (F8B...F9A = 2.87 (1) Å) and is not unusually short. The mixed alkoxide hexafluoroacetylacetonate is clearly a dimer with bridging methoxy groups and terminal, bidentate oxygen-bonded F₆acac ligands. The two palladium atoms, Pd1 and Pd2, are in approximately square-planar environments comprised by the four

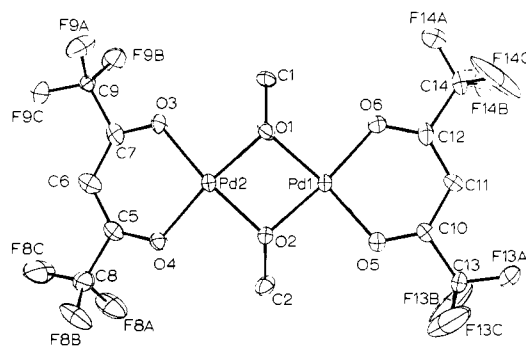


Figure 1. ORTEP drawing of the molecular structure of Pd₂(μ-CH₃O)₂(F₆acac)₂ showing the labeling scheme. Ellipsoids are drawn with 30% probability boundaries.

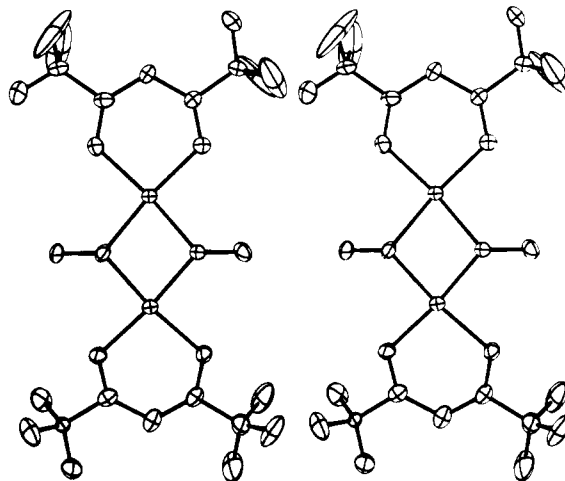


Figure 2. ORTEP stereoview of the molecule.

surrounding oxygen atoms and are displaced by 0.077 (1) and 0.027 (1) Å, respectively, from the least-squares planes which contain O1, O2, O5, O6 and O1, O2, O3, O4. A table of weighted least-squares planes is available as supplementary material. The molecular geometry is shown in Figures 1 and 2, and selected distances and angles are given in Table I. The four corresponding O-Pd-O angles around Pd1 and Pd2 are the same within experimental error and exemplify the pseudo-twofold symmetry of the molecular structure. The F₆acac chelate bite angles [O5-Pd1-O6 = 94.1 (2) and O3-Pd2-O4 = 94.9 (2)°] are somewhat large compared with those found in other structures which contain the (F₆acac)Pd moiety.^{1,2} The Pd1-O1-Pd2 and Pd1-O2-Pd2 angles are 97.1 (2) and 96.5 (2)°, respectively, and the O1-Pd1-O2 and O1-Pd2-O2 angles are 79.4 (2) and 80.2 (2)°. The O1...O2 distance [2.56 (1) Å] is considerably shorter than the separations between O3...O4 [2.93 (1) Å] and O5...O6 [2.93 (1) Å], and the distance between palladium atoms is 2.984 (1) Å. This distance and the overall geometry of the Pd₂O₂ ring argue against any significant metal-metal bonding in 1. The Pd₂O₂ ring is folded along the O1-O2 vector so that the dihedral angle between the Pd1, O1, O2 and Pd2, O1, O2 planes is 26°. The two halves of the molecule which are related by the pseudo-twofold axis are each approximately planar; however, packing forces are responsible for slight deviations. For example, the dihedral angle between the least-squares planes which contain O5, O6, C10, C11, C12 and O1, O2, O5, O6 is 10.5°. The dihedral angle between the corresponding pseudo-C₂-related planes [O3, O4, C5, C6, C7 and O1, O2, O3, O4] is only 1.6°.

The four Pd-O distances in the Pd₂O₂ unit range from 1.982 (7) to 2.005 (7) Å. The average distance involving the bridging methoxy group is 1.996 (7) Å, and *d*(Pd-O)_{av} involving the F₆acac ligands has the same value within experimental error

Table I. Selected Distances and Angles^a

| | | Distances, Å | | | |
|-----------|-----------|--------------|-----------|------------------------|-----------|
| Pd1-Pd2 | 2.984 (1) | O3-C7 | 1.27 (1) | C5-C8 | 1.53 (1) |
| Pd1-O1 | 2.001 (7) | O4-C5 | 1.28 (1) | C7-C9 | 1.52 (1) |
| Pd2-O1 | 1.982 (7) | O5-C10 | 1.26 (1) | C10-C13 | 1.50 (1) |
| Pd1-O2 | 2.005 (7) | O6-C12 | 1.27 (1) | C12-C14 | 1.53 (1) |
| Pd2-O2 | 1.994 (7) | O1-C1 | 1.47 (1) | C8-F ^b | 1.32 (2) |
| Pd1-O5 | 2.003 (7) | O2-C2 | 1.46 (1) | C9-F ^b | 1.33 (2) |
| Pd1-O6 | 1.999 (7) | C5-C6 | 1.38 (1) | C13-F ^b | 1.28 (2) |
| Pd2-O3 | 1.986 (7) | C6-C7 | 1.42 (1) | C14-F ^b | 1.28 (2) |
| Pd3-O2 | 1.984 (7) | C10-C11 | 1.43 (1) | O1-O2 | 2.56 (1) |
| | | C11-C12 | 1.39 (1) | O3-O4 | 2.93 (1) |
| | | | | O5-O6 | 2.93 (1) |
| | | Angles, Deg | | | |
| O1-Pd1-O2 | 79.4 (2) | Pd1-O5-C10 | 122.2 (7) | O5-C10-C11 | 130 (1) |
| O1-Pd1-O2 | 80.2 (2) | Pd1-O6-C12 | 121.3 (7) | O6-C12-C11 | 131 (1) |
| O5-Pd1-O6 | 94.1 (2) | Pd2-O3-C7 | 121.9 (7) | O3-C7-C9 | 111.7 (8) |
| O1-Pd1-O6 | 93.1 (2) | Pd2-O4-C5 | 121.0 (7) | O4-C5-C8 | 112 (1) |
| O2-Pd1-O5 | 93.0 (2) | Pd1-O1-Pd2 | 97.1 (2) | O5-C10-C13 | 113.9 (8) |
| O1-Pd1-O5 | 171.4 (2) | Pd1-O2-Pd2 | 96.5 (2) | O6-C12-C14 | 114 (1) |
| O2-Pd1-O6 | 171.5 (2) | Pd1-O1-C1 | 120.2 (6) | C5-C8-F ^b | 111 (1) |
| O3-Pd2-O4 | 94.9 (2) | Pd2-O1-C1 | 118.2 (6) | C7-C9-F ^b | 112 (1) |
| O1-Pd2-O3 | 92.9 (2) | Pd1-O2-C2 | 120.5 (6) | C10-C13-F ^b | 114 (1) |
| O2-Pd2-O4 | 92.0 (2) | Pd2-O2-C2 | 118.2 (6) | C12-C14-F ^b | 113 (1) |
| O1-Pd2-O4 | 171.9 (2) | O3-C7-C6 | 130 (1) | F-C-F ^b | 106 (1) |
| O2-Pd2-O3 | 173.0 (2) | O4-C5-C6 | 131 (1) | C5-C6-C7 | 121 (1) |
| | | | | C10-C11-C12 | 121 (1) |

^a The numbers in parentheses are the esd's of the last significant figure. ^b Value is average involving all equivalent fluorine atoms.

[1.993 (7) Å]. These Pd-O distances may be compared with 2.014 (6) and 1.996 (7) in [(bpy)Pd(F₆acac)]F₆acac,² 2.099 (5) in the dichloromethane solvate of chloro[1-(diphenylphosphino)-3,3,3-trifluoropropen-2-olato](ethoxydiphenylphosphine)palladium¹¹ and 2.03 Å in the dioxane solvate of chloro[1-(2-thiazolylazo)-2-naphtholato]palladium.¹² The O₂C₃ atoms which form the F₆acac chelate rings are coplanar within experimental error, and the Pd1 and Pd2 atoms are displaced 0.172 (1) and 0.063 (1) Å from their respective planes. Compared with ionic F₆acac in (4-ClC₃H₄N)₄Pd(F₆acac)₂,⁴ where *d*(C-O)_{av} is 1.23 (1) Å and <C-C-C_{av} is 124 (1)°, the average C-O distance [1.27 (1) Å] is longer and the average ring C-C-C angle has contracted to 121 (1)°.

Reactions of Pd₂(μ-CH₃O)₂(F₆acac)₂. Thermal decomposition of crystalline **1** is formally a disproportionation reaction and yielded palladium metal and Pd(F₆acac)₂. This is somewhat surprising since the F₆acac ligands are well separated in the solid state. The methoxy bridging groups appeared as methanol and methyl formate along with small and variable amounts of dimethoxymethane. Qualitatively, these organic products can be accounted for by proposing that methanol arises from cleavage of the Pd-OCH₃ bonds, forming methoxy radicals which abstract hydrogen from the F₆acac groups and that β elimination from the μ-OCH₃ moiety generates formaldehyde. Dimethoxymethane is just the dimethyl acetal of formaldehyde and dehydrogenation of the hemiacetal of formaldehyde and methanol would provide methyl formate. In support of this, vacuum pyrolysis of Pd₂(μ-CD₃O)₂(F₆acac)₂ produced CD₃OH and DC(O)OCD₃. It should be emphasized that the thermolysis reaction is heterogeneous and probably very complicated owing to the presence of finely divided metallic palladium. The decomposition of both formaldehyde and methanol on clean polycrystalline palladium is known to be rapid at 27 °C.¹³ Indeed, the bridging methoxy groups in **1** provide a plausible model for intermediate surface methoxy groups in the dehydrogenation of methanol on metals. Those on palladium are so unstable as to have eluded detection,

but ultraviolet photoemission spectroscopy has furnished evidence for a possible surface methoxy group on Ni(111).¹⁴ The relative ease of hydrogen transfer to late second- and third-row metals may account for the paucity of alkoxide chemistry of these elements¹⁵ although methoxy-bridged Pt₂(μ-Cl)(μ-CH₃O)(*t*-Bu₂PCMe₂CH₂)₂ has been reported.¹⁶

Reaction of Pd(F₆acac)₂ with Alcohols. The formation of **1** presumably involves as an intermediate an adduct of Pd(F₆acac)₂ with the Lewis base methanol. The adduct has low stability since evaporation of methanolic Pd(F₆acac)₂ yielded only pure Pd(F₆acac)₂. However, the infrared spectra of the alcohol solutions showed a carbonyl group mode at 1688 ± 1 cm⁻¹ vs. 1603 ± 1 cm⁻¹ in chloroform. This shift to higher frequency is typical for Lewis base adducts of Pd(F₆acac)₂¹⁻⁴ and suggests that a weak complex is formed in solution.

Efforts to prepare homologues of **1** failed perhaps due to their higher solubility or the instability of palladium alkoxides in which the alkoxy group has an abstractable hydrogen atom. So that this point could be explored, the reactions of Pd(F₆acac)₂ with an exemplary simple aliphatic alcohol, 1-propanol, were studied in more detail. The products depend markedly on whether or not oxygen is present. When Pd(F₆acac)₂ was heated with excess degassed 1-propanol, slow reduction of the metal chelate to form palladium metal occurred. The organic products consisted of propyl propionate, propyl propenyl ether, and ethyl propionate. Some of the hexafluoroacetylacetonate ligands were degraded and emerged as propyl trifluoroacetate. Under an atmosphere of oxygen, the yields of propyl propionate and propyl trifluoroacetate were greatly increased and significant amounts of propionaldehyde were also formed. These results are explicable in terms of a palladium-catalyzed oxidation of 1-propanol to propionaldehyde and propionic acid. Esterification of the carboxylic acid by the (excess) propanol would lead to propyl propionate, and dehydration of the hemiacetal formed from propanol and propionaldehyde would provide propyl propenyl ether. The molar ratio of propanol to propyl propionate changes from 92:1

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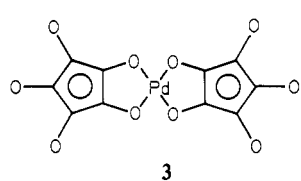
Table II. Positional Parameters and Their Estimated Standard Deviations^a

| atom | x | y | z | B _{iso,eq} , Å ² | atom | x | y | z | B _{iso,eq} , Å ² |
|------|--------------|------------|-------------|--------------------------------------|------|--------------|------------|-------------|--------------------------------------|
| Pd1 | -0.05453 (8) | 0.1941 (1) | 0.34114 (3) | 1.510 | Pd2 | 0.00571 (9) | 0.1633 (1) | 0.24270 (3) | 1.446 |
| F8A | 0.4222 (7) | 0.374 (1) | 0.1726 (3) | 4.396 | F13A | 0.1034 (9) | 0.233 (2) | 0.5149 (3) | 11.502 |
| F8B | 0.4308 (7) | 0.082 (1) | 0.1628 (3) | 4.176 | F13B | 0.2252 (11) | 0.401 (1) | 0.4752 (3) | 9.395 |
| F8C | 0.3524 (8) | 0.262 (2) | 0.1079 (3) | 7.341 | F13C | 0.2488 (10) | 0.120 (1) | 0.4720 (3) | 8.010 |
| F9A | -0.2908 (7) | 0.088 (1) | 0.1083 (2) | 3.432 | F14A | -0.5044 (7) | 0.244 (2) | 0.4030 (3) | 5.793 |
| F9B | -0.2884 (7) | 0.382 (1) | 0.1178 (2) | 3.265 | F14B | -0.4183 (10) | 0.404 (2) | 0.4540 (4) | 12.589 |
| F9C | -0.1518 (7) | 0.260 (1) | 0.0689 (2) | 3.901 | F14C | -0.4181 (9) | 0.127 (2) | 0.4619 (4) | 15.029 |
| O1 | -0.1649 (7) | 0.130 (1) | 0.2816 (2) | 1.762 | O4 | 0.1945 (7) | 0.184 (1) | 0.2113 (2) | 1.835 |
| O2 | 0.1171 (7) | 0.131 (1) | 0.3034 (2) | 1.820 | O5 | 0.0794 (8) | 0.231 (1) | 0.3979 (2) | 2.173 |
| O3 | -0.1276 (8) | 0.186 (1) | 0.1860 (2) | 1.909 | O6 | -0.2431 (7) | 0.230 (1) | 0.3729 (3) | 2.309 |
| C1 | -0.307 (1) | 0.224 (2) | 0.2678 (4) | 2.370 | C9 | -0.201 (1) | 0.237 (2) | 0.1100 (4) | 1.959 |
| C2 | 0.261 (1) | 0.226 (2) | 0.3114 (4) | 2.243 | C10 | 0.029 (1) | 0.242 (2) | 0.4367 (4) | 1.890 |
| C5 | 0.192 (1) | 0.213 (2) | 0.1681 (4) | 1.980 | C11 | -0.122 (1) | 0.248 (2) | 0.4492 (4) | 2.510 |
| C6 | 0.074 (1) | 0.229 (1) | 0.1354 (4) | 2.113 | C12 | -0.241 (1) | 0.242 (2) | 0.4159 (4) | 2.225 |
| C7 | -0.076 (1) | 0.215 (1) | 0.1475 (4) | 1.833 | C13 | 0.148 (1) | 0.250 (2) | 0.4751 (4) | 2.214 |
| C8 | 0.351 (1) | 0.232 (2) | 0.1517 (4) | 2.911 | C14 | -0.396 (1) | 0.252 (2) | 0.4342 (4) | 2.966 |

^a All atoms refined with anisotropic thermal parameters; equivalent isotropic thermal parameters are listed.

under anaerobic conditions to 3.3:1 when oxygen was present, under which conditions ester synthesis is quite facile.

Earlier, we proposed that Pd(F₆acac)₂ reacted with alumina to form a surface compound (F₆acac)Pd(HOAl-)₂⁺, where HOAl- represents a surface hydroxy group attached to aluminum.⁶ Because reactions of Pd(F₆acac)₂ with oxygen donors has received little attention thus far, we examined that with croconate, C₅O₅²⁻, a nonreducing oxyanion. Condensation of (PPN)₂C₅O₅·2H₂O [PPN = bis(triphenylphosphine)iminium-(1+)] with Pd(F₆acac)₂ led to the displacement of both F₆acac ligands and the formation of (PPN)₂[(C₅O₅)₂Pd] (3). This



compound behaves as a 2:1 electrolyte in nitromethane. Its ¹³C NMR spectrum in dichloromethane showed, in addition to PPN resonances, three peaks of relative areas 1:2:2 at 182.1, 190.2, and 198.4 ppm, indicating that croconate functions as a η²-oxygen-bonded ligand as has been proposed for first-row transition-metal complexes of C₅O₅²⁻^{17,18} and for partially oxidized bis(squarato)platinum(II) salts.¹⁹

Experimental Section

Infrared spectra were obtained on Nujol mulls with an instrument with grating optics; frequencies of peak maxima are believed to be accurate to within 5 cm⁻¹. Spectra in the 3300–1900-cm⁻¹ range were also recorded with KBr pellets and those in methanol solution on a Nicolet Digilab Fourier transform interferometer with an accuracy of ±1 cm⁻¹. A Varian XL-100 spectrometer was used to obtain NMR spectra. Chemical shifts are relative to internal (CH₃)₄Si (¹H and ¹³C) or CFC₃ (¹⁹F). Electron impact mass spectra (70 eV) were obtained on a Du Pont 21-491B spectrometer. This was interfaced with a Varian 2740 gas chromatograph fitted with a 2-ft. Porapak Q column. The chromatograph was programmed to operate at 50–250 °C, increasing at 15 °C min⁻¹ with the FID detector kept at 280 °C.

Pd₂(μ-CH₃O)₂(F₆acac)₂ (1). A solution of 0.31 g (0.6 mol) of Pd(F₆acac)₂ in about 1.5 mL of methanol was allowed to stand overnight at room temperature. The title compound, 0.08 g (0.12 mmol, 40%) separated as rust-colored crystals which were collected on a filter, washed with methanol, and vacuum-dried. It was stored at -20 °C. Evaporation of the filtrate and vacuum sublimation of the residue afforded recovered Pd(F₆acac)₂, 0.13 g. Anal. Calcd for C₁₂H₈F₁₂O₆Pd₂: C, 20.9; H, 1.2; F, 33.1, Pd, 30.0. Found: C, 20.9;

H, 1.1; F, 33.0; Pd, 31.2. IR: 3120 (w), 1625 (m), 1610 (s), 1600 (s), 1555 (m), 1470 (s), 1430 (m), 1350 (m), 1270 (m), 1120 (s), 1010 (m), 805 (s), 750 (w), 700 (m), 600 (m), 585 (m) and 430 (w) cm⁻¹.

Pd₂(μ-CD₃O)₂(F₆acac)₂ (2) was similarly prepared by using CD₃OD instead of CH₃OH. IR: 3200 (w), 2070 (w), 1605 (s), 1525 (m), 1450 (s), 1350 (m), 1280 (s), 1220 (s), 1165 (s), 1115 (s), 985 (m), 770 (m), 695 (m), 590 (m), and 555 (m) cm⁻¹.

(PPN)₂[(C₅O₅)₂Pd] (3). Potassium croconate, 1.9 g, was dissolved in hot water and to it was added 9.2 g of PPN⁺Cl⁻ in 150 mL of hot water. The resulting bright yellow precipitate was collected on a filter, washed with water, and dried at 10⁻³ mm. The yield of (PPN)₂·C₅O₅·2H₂O was 8.8 g. Anal. Calcd for C₇₇H₆₄N₂O₇P₄: C, 73.8; H, 5.1; N, 2.2. Found: C, 74.2; H, 5.2; N, 2.2. The infrared spectrum showed a band at 3400 cm⁻¹ attributed to water of crystallization.

A 1-mmol (1.22-g) sample of (PPN)₂C₅O₅·2H₂O was dissolved in 30 mL of ethanol, and 0.5 mmol (0.26 g) of Pd(F₆acac)₂ in 10 mL of the same solvent was added. The crude product, 1.10 g, separated as a yellow precipitate. Recrystallization from hot acetonitrile provided 0.72 g of pure (PPN)₂[(C₅O₅)₂Pd] as shiny brown plates: mp 224–225 °C with some decomposition; IR 1735 (w), 1630 (s), 1470 (s), 1440 (m), 1265 (s), 1120 (m), 730 (m), 630 (w), 550 (m), 540 (m), 400 (w), and 290 (m) cm⁻¹; electronic spectrum (CHCl₃) λ_{max} at 365 (log ε 4.51) and 410 (4.61) nm; molar conductivity of a 7.6 × 10⁻² M solution in nitromethane 102 Ω⁻¹ cm² mol. Anal. Calcd for C₈₂H₆₀N₂O₁₀PdP₄: C, 67.3; H, 4.1; N, 1.9. Found C, 67.1; H, 4.1; N, 1.8.

Pyrolysis of Pd₂(μ-CH₃O)₂(F₆acac)₂. A 0.065-g sample of 1, contained a continuously evacuated sublimator fitted with a -78 °C cold finger, was heated with a 110 °C oil bath until decomposition of the compound was complete. The sublimate weighed 0.032 g and was found by infrared and mass spectroscopic analyses to be Pd-(F₆acac)₂ contaminated with a trace of methanol. The dark, fluffy nonvolatile residue weighed 0.0093 g. Chemical analysis revealed that it was 98.4% palladium. Thus, the yields of Pd(F₆acac)₂ and palladium were 0.06 mmol (67%) and 0.88 mmol (98% of theory).

In another experiment, 0.03 g of the palladium methoxide was sealed under high vacuum into a small glass tube fitted with a break seal. After 30 min of heating at 105 °C, the tube was cooled to room temperature and opened via the break-seal directly into the gas chromatograph-mass spectrometer. In this experiment, the volatiles consisted of about 72% methanol, 26% methyl formate, and 2% dimethoxymethane.

Reaction of Pd(F₆acac)₂ with 1-Propanol. A 0.25-g quantity of Pd(F₆acac)₂ and 0.9 mL of 1-propanol were placed in a 50-mL glass bulb fitted with a vacuum stopcock. The mixture was degassed by four freeze-pump-thaw cycles on a high-vacuum line and then heated for 16 h in a 95 °C oil bath, during which time, metallic palladium separated. The organic compounds formed were analyzed by GC-MS and quantitated by gas chromatography on a 1/8 in. × 7 ft column of 80–100 mesh Porapak Q. The injector and thermal conductivity detector were maintained at 200 and 230 °C, respectively; the column was heated from 100 to 220 °C at a rate of 10 °C min⁻¹ and held at 220 °C for 5 min. Product yields, normalized to 1-propanol, were

(17) R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **85**, 2589 (1963).

(18) R. West and H. Y. Niu, *J. Am. Chem. Soc.*, **85**, 2586 (1963).

(19) H. Toftlund, *J. Chem. Soc., Chem. Commun.* 837 (1979).

as follows: ethyl propionate, 0.015; propionaldehyde, <0.002; propanol, 1.00; propyl trifluoroacetate, 0.022; propyl propenyl ether, 0.036; propyl propionate, 0.018.

A similar experiment was carried out in which the glass bulb was flushed with oxygen prior to sealing and heating the reactants. Analysis as before gave the following normalized yields: propionaldehyde, 0.14; propanol, 1.00; propyl trifluoroacetate, 0.14; propyl propionate, 0.50.

Structure Determination. A rectangular crystal of $\text{Pd}_2(\mu\text{-CH}_3\text{O})_2(\text{F}_6\text{acac})_2$ (formula weight 689.0) having approximate dimensions $0.31 \times 0.22 \times 0.055$ mm was selected from those produced in the preparative synthetic reaction and used in the structure determination. The crystal was found to belong to the monoclinic crystal class by the Enraf-Nonius CAD4-SPD peak search, centering and indexing programs. The space group $P2_1/c$ (No. 14) was chosen on the basis of systematic absences observed during data collection and was verified by successful solution and refinement (*vide infra*). The unit cell dimensions were determined at 23 °C by least-squares refinement of the angular settings of 25 peaks centered on the diffractometer and are $a = 8.945$ (4) Å, $b = 7.149$ (6) Å, $c = 29.36$ (1) Å, $\beta = 93.89$ (3)°, and $V = 1873$ Å³. The calculated density is 2.443 g/cm³ 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 use of 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 1.5 h of X-ray exposure, and no decay with time was noted. Intensities of 2592 unique reflections ($+h$, $+k$, $\pm l$) were measured at room temperature out to 2θ of 50° with Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å). After correction for Lorentz, polarization, background, and absorption ($\mu = 20.4$ cm⁻¹, maximum and minimum transmission factors 0.897 and 0.653) effects,²⁰ 2021

reflections were judged observed [$F_o^2 \geq 2.0\sigma(F_o^2)$] and were used in all subsequent calculations.²¹

Conventional heavy-atom techniques were used to solve the structure, and the final refinement was carried out with all nonhydrogen atoms thermally anisotropic by full-matrix least-squares methods (290 variables). R and R_w converged to their final values of 0.057 and 0.067, respectively.²² The error in an observation of unit weight was determined to be 2.22 by using a value of 0.04 for p in the $\sigma(I)$ equation.²⁰

The final atomic coordinates with their esd's are given in Table II. 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, and an ORTEP stereoview is presented in Figure 2.

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Registry No. 1, 81602-81-5; 2, 81602-82-6; 3, 81616-03-7; Pd(F_6acac)₂, 64916-48-9; 1-propanol, 71-23-8.

Supplementary Material Available: Listings of structure factor amplitudes, anisotropic thermal parameters, and least-squares planes (11 pages). Ordering information is given on any current masthead page.

(20) The intensity data were processed as described in the "CAD4 and SDP Users Manual", Enraf-Nonius, Delft, Holland, 1978. The net intensity is given as $I = (K/NPI)(C - 2B)$, where $K = 20.1166$ times the 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 $\sigma(F_o) = 1/2(\sigma(I)/I)F_o$.

(21) All calculations were carried out on a PDP 11/34 computer using the Enraf-Nonius SDP programs. This crystallographic computing package is described in B. A. Frenz, "The Enraf-Nonius CAD 4 SPD-A Real Time System for Concurrent X-Ray Data Collection and Crystal Structure Determination" 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.

(22) The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The unweighted and weighted residuals are $R = (\sum ||F_o| - |F_c||) / \sum |F_o|$ and $R_w = [(\sum w(|F_o| - |F_c|)) / (\sum w|F_o|)^2]^{1/2}$. 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.