The 75-MHz ^{13}C{^{1}H} NMR data are presented in Table VI. Assignments were made consistent with earlier data of Bundesgaard and Jakobsen,[19] and with the aid of ^{1}H/^{13}C heteronuclear chemical shift correlated (HETCOR) NMR experiments. Figure 2 shows the HETCOR spectrum of [PhP(CH=CH$_2$)$_2$]$_2$PdBr$_2$. The correlations for the H$_a$–C$_\alpha$ nuclei in the HETCOR spectra indicate that $^2J_{PH}$ and $^1J_{PC_\alpha}$ are of like sign.[20] Several trends in the data are notable. Upon coordination, the phenyl ortho and para carbon resonances of both ligands, Ph$_2$PCH=CH$_2$ and PhP(CH=CH$_2$)$_2$, shift downfield and the meta carbon resonances remain essentially unchanged. The phenyl ipso carbon resonances for the L$_2$PdCl$_2$ and L$_2$PdBr$_2$ complexes experience a large upfield shift of 9–10 ppm upon coordination, and a 6–7 ppm upfield shift is noted for the L$_2$PdI$_2$ complexes. The large upfield shift may be attributed to π-back-bonding between palladium and the vinylphosphines with the phenyl group acting as an electron sink.

Upon coordination the resonances for the α-carbons of the vinyl group shift upfield, while the β-carbon resonances shift downfield, except for a slight upfield shift for the β-carbon in *trans*-(Ph$_2$PCH=CH$_2$)$_2$PdCl$_2$. This polarization of the C=C double bond is also likely a result of π-back-bonding. For alkylphosphines,[21] coordination induces an upfield shift in both the α- and β-carbon resonances. The downfield shift noted for the β-carbon resonances in the (Ph$_2$PCH=CH$_2$)$_2$PdX$_2$ and [PhP-(CH=CH$_2$)$_2$]$_2$PdX$_2$ complexes was also observed for the platinum analogues[18,22] as well as for platinum[23] and palladium[24] phosphole

complexes. This anomalous downfield shift for the resonance of the β-carbons of the phosphole complexes has been attributed[23] to a (2p–3d) interaction between the phosphole ring butadiene moiety and phosphorus. This explanation has been extended to explain the small coordination chemical shifts for phosphines having unsaturated groups that may conjugate with phosphorus in similar ways.[25-27]

Ligand Polarization and Diels–Alder Reactivity. With the characterization of the palladium vinylphosphine and phosphole[24] complexes complete it becomes evident that significant polarization of the C=C double bond occurs for both the vinylphosphine and phosphole ligands upon coordination. It appears that polarization of both the vinyl group of the phosphine and the phosphole are necessary for the intramolecular Diels–Alder [4 + 2] cycloaddition reactions[1] of Pd and Pt vinylphosphine and phosphole complexes to occur. This information should aid in better understanding the mechanism for these [4 + 2] cycloaddition reactions, which will be discussed in a future publication.

Registry No. *cis*-(Ph$_2$PCH=CH$_2$)$_2$PdCl$_2$, 113214-83-8; *trans*-(Ph$_2$PCH=CH$_2$)$_2$PdCl$_2$, 98717-39-6; *cis*-(Ph$_2$PCH=CH$_2$)$_2$PdBr$_2$, 113109-73-2; *trans*-(Ph$_2$PCH=CH$_2$)$_2$PdBr$_2$, 113214-84-9; *trans*-(Ph$_2$PCH=CH$_2$)$_2$PdI$_2$, 113109-74-3; *cis*-[PhP(CH=CH$_2$)$_2$]$_2$PdCl$_2$, 98651-93-5; *trans*-[PhP(CH=CH$_2$)$_2$]$_2$PdCl$_2$, 98717-40-9; *cis*-[PhP-(CH=CH$_2$)$_2$]$_2$PdBr$_2$, 113109-75-4; *trans*-[PhP(CH=CH$_2$)$_2$]$_2$PdBr$_2$, 113214-85-0; *trans*-[PhP(CH=CH$_2$)$_2$]$_2$PdI$_2$, 113109-76-5; (PhCN)$_2$PdCl$_2$, 14220-64-5; Ph$_2$PCH=CH$_2$, 2155-96-6; PhP(CH=CH$_2$)$_2$, 26681-88-9.

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# Interconversion of Dinuclear and Oxo-Centered Trinuclear Cobaltic Acetates

Charles E. Sumner, Jr.

Reaction of the oxo-centered cobalt cluster [(py)$_3$Co$_3$O(OAc)$_5$OH]$^+$, [5]$^+$, with water in acetic acid produces a dinuclear cluster, [(py)$_4$Co$_2$(OAc)$_3$(OH)$_2$]$^+$, [3]$^+$, and a new oxo-centered cluster, [(py)$_5$Co$_3$O(OAc)$_3$(OH)$_2$]$^{2+}$, [4]$^{2+}$, as an equilibrium mixture. The clusters [3]$^+$ and [4]$^{2+}$ were also synthesized by the oxidation of cobaltous acetate with peracetic acid in the presence of pyridine in aqueous acetic acid. Treatment of [3]$^+$ and [4]$^{2+}$ with glacial acetic acid gives a mixture of [5]$^+$ and [(py)$_3$Co$_3$O(OAc)$_6$]$^+$, [6]$^+$. [3][PF$_6$] and [4][PF$_6$]$_2$ were characterized by X-ray crystallographic techniques. At 20 ± 1 °C, crystals of both compounds are monoclinic, with a = 12.478 (2) Å, b = 14.223 (3) Å, c = 23.278 (4) Å, β = 103.92 (1)°, V = 4010 (1) Å^3, Z = 4 [μ_a(Mo Kα) = 1.21 mm^{-1}], and space group $P2_1/c$-C_{2h} for [3][PF$_6$], and with a = 16.500 (3) Å, b = 17.128 (4) Å, c = 17.357 (4) Å, β = 105.64 (2)°, V = 4724 (2) Å^3, Z = 4 [μ_a(Mo Kα) = 1.32 mm^{-1}], and space group $P2_1/n$ for [4][PF$_6$]$_2$.

Recently, there has been a renewed interest in transition-metal-catalyzed autoxidation reactions. In these reactions, the transition-metal is believed to be responsible for chain initiation and the decomposition of various peroxides formed during the reaction.[1] Perhaps the most studied autoxidation system over the last 20 years is the cobalt-catalyzed oxidation of aromatic hydrocarbons;[2] however, the active form of cobalt in this system is still unknown although several structures have been proposed. For example, Koubek and Edwards[3] proposed the neutral, dinuclear structure [1] for a green, amorphous solid obtained by the
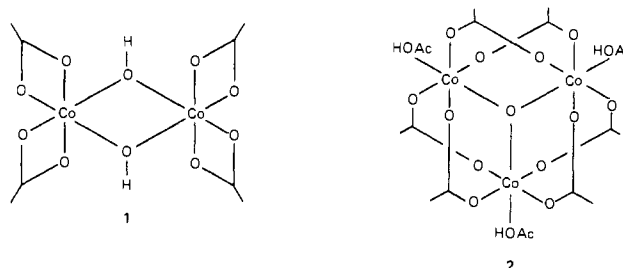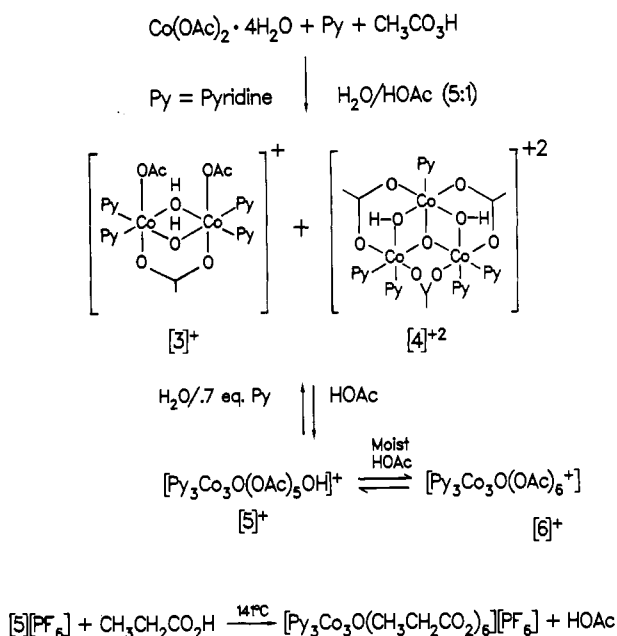

oxidation of cobaltous acetate with peracetic acid. The same structure was proposed by Kochi[4] for cobaltic acetate obtained

(1) (a) Scott, E. J. Y. *J. Phys. Chem.* **1970**, *74*, 1174. (b) Hendriks, C. F.; van Beek, H. C. A.; Heertjes, P. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1979**, *18*, 38.
(2) (a) Hieba, E. I.; Dessau, R. M.; Koehl, W. J., Jr. *J. Am. Chem. Soc.* **1969**, *91*, 6830. (b) Hendriks, C. F.; van Beek, H. C. A.; Heertjes, P. M. *Ind. Eng. Chem. Prod. Res. Dev.* **1978**, *17*, 256 and references cited therein.

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Scheme I

Figure 1. Perspective ORTEP drawing of the $[(py)_4Co_2(OAc)_3(OH)_2]^+$ cation in crystalline $[(py)_4Co_2(OAc)_3(OH)_2][PF_6]\cdot2CH_2Cl_2$. The Co atoms are represented by 50% probability ellipsoids, and the remaining atoms are represented by arbitrarily sized spheres for purposes of clarity.
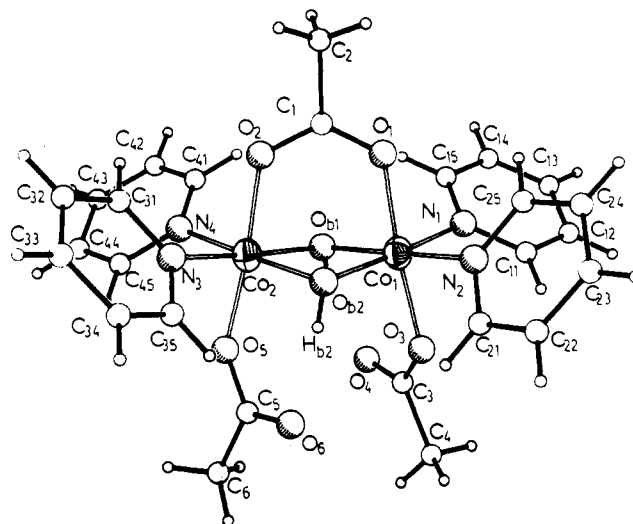
by the ozonation of cobaltous acetate. However Ziolkowski[5] et al. proposed the neutral, mixed-valence, oxo-centered structure [2] for the product from ozonation of cobaltous acetate in anhydrous acetic acid. Recently, Jones[6] has shown through the use of visible spectroscopy that at least three different forms of cobaltic acetate are present in solution and has suggested that two of the complexes are in equilibrium and have structures similar to [1] and [2]. During the course of our studies on model complexes related to autoxidation catalysts,[7] we have found several oxo-centered cluster complexes whose synthesis and interconversion are reported here.
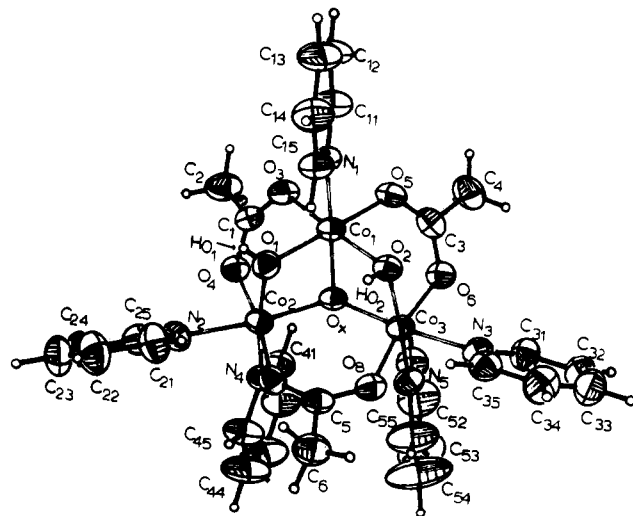
Results

Salts of the clusters [3]$^+$ and [4]$^+$ were synthesized as shown in Scheme I. Treatment of a solution of cobaltous acetate and pyridine in aqueous acetic acid with 35% peracetic acid followed by slowly heating the mixture to reflux produced a mixture of [3]$^+$ and [4]$^+$. The complexes were precipitated by the addition of NH_4PF_6 and were separated by extracting the resulting solid mixture with methylene chloride. The [PF$_6$]$^-$ salt of dinuclear cluster [3]$^+$ is soluble in methylene chloride whereas that of [4]$^+$ is not. The residue was recrystallized from acetonitrile/ether to give the [PF$_6$]$^-$ salt of the trinuclear cluster [4]$^{2+}$. Both compounds were characterized by X-ray crystallographic[8] techniques, ^{1}H NMR spectroscopy (400 MHz), and fast atom bombardment mass spectroscopy.

The ratio of [3]$^+$ to [4]$^{2+}$ shown in Scheme I is independent of the length of time the mixture is heated, denoting an equilibrium condition. The composition of the mixtures was determined by ^{1}H NMR spectroscopy following precipitation of the salts as mentioned above. Attempts to observe the equilibrium directly by ^{1}H NMR spectroscopy were unsuccessful due to small amounts of paramagnetic cobalt(II) species in solution. If the amount of water is increased to 90%, then no [5]$^+$ is detected. Interestingly, treatment of [5][PF$_6$] with aqueous acetonitrile (20% water) produces the trinuclear cluster [4][PF$_6$]$_2$ in good yield but does not give any of the dinuclear compound. If pyridine is omitted from the example shown in Scheme I, then the amount of [5]$^+$

(4) Lande, S. S.; Falk, C. D.; Kochi, J. K. *J. Inorg. Nucl. Chem.* **1971**, *33*, 4101.
(5) Ziolkowski, J. J.; Pruchnik, F.; Szymanska-Buzar, T. *Inorg. Chim. Acta* **1973**, *7*, 473.
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(8) The structural determinations were carried out at the Crystalytics Co., Lincoln, NE.

Figure 2. Perspective ORTEP drawing of the $[(py)_5Co_3O(OAc)_3(OH)_2]^{2+}$ cation in crystalline $[(py)_5Co_3O(OAc)_3(OH)_2][PF_6]_2\cdot CH_2Cl_2\cdot H_2O$. Non-hydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; hydrogen atoms are represented by arbitrarily small spheres.

in the final mixture is increased while the amounts of [3]$^+$ and [4]$^{2+}$ are decreased, and the reaction is accompanied by considerable decomposition to cobalt(II), suggesting that pyridine is necessary to stabilize the new clusters. Reaction of either the dinuclear cluster [3]$^+$ or the trinuclear cluster [4]$^{2+}$ with acetic acid regenerates [5]$^+$ in good yield. The cluster [5]$^+$ is in equilibrium with the trinuclear hexaacetate $[(py)_3Co_3O(OAc)_6]^+$, [6]$^+$, in moist acetic acid.

The acetate ligands of the cluster framework can be exchanged under fairly mild conditions. For example, treatment of [5][PF$_6$] with acetic-d_3 acid-d at 70 °C for 30 min results in the complete replacement of proteated acetate ligands with deuteriated ligands. Other carboxylic acids can be used to displace the acetate ligands. This is illustrated by the reaction of [5][PF$_6$] with hot propionic acid to give $[(py)_3Co_3O(CH_3CH_2CO_2)_6][PF_6]$.

Solid-State Structures of $[(py)_4Co_2(OAc)_3(OH)_2][PF_6]\cdot2CH_2Cl_2$, [3][PF$_6$], and $[(py)_5Co_3(OAc)_3(OH)_2][PF_6]_2\cdot CH_2Cl_2\cdot H_2O$, [4][PF$_6$]$_2$. X-ray structural analyses revealed that single crystals of [3][PF$_6$] are composed of discrete dinuclear $[(py)_4Co_2(OAc)_3(OH)_2]^+$ cations (Figure 1), [PF$_6$]$^-$ anions (supplementary Figure S1), and CH_2Cl_2 solvent molecules of crystallization (supplementary Figure S2). The single crystals of [4][PF$_6$]$_2$ are composed of discrete trinuclear $[(py)_5Co_3O(OAc)_3(OH)_2]^{2+}$ cations (Figure 2), PF$_6$$^-$

Table I. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline [Co₂(OH)₂(O₂CCH₃)₃(NC₅H₅)₄][PF₆]·2CH₂Cl₂[a]

atom type[b]	fractional coordinates			equiv isotropic thermal param, B, Å² × 10[c]
	$10^4 x$	$10^4 y$	$10^4 z$	
	Cation			
Co₁	1754 (1)	1838 (1)	3824 (1)	28 (1)
Co₂	1748 (1)	3814 (1)	3819 (1)	28 (1)
O_{b1}	1024 (2)	2827 (2)	4119 (1)	30 (1)
O_{b2}	2658 (2)	2824 (2)	3673 (1)	29 (1)
O₁	797 (2)	2024 (2)	3055 (1)	34 (1)
O₂	761 (2)	3607 (2)	3063 (1)	35 (1)
O₃	2749 (2)	1538 (2)	4552 (1)	33 (1)
O₄	1928 (3)	2229 (2)	5191 (1)	48 (1)
O₅	2629 (2)	4139 (2)	4573 (1)	35 (1)
O₆	4159 (2)	3276 (2)	4651 (1)	43 (1)
N₁	748 (3)	890 (2)	3987 (1)	32 (1)
N₂	2588 (3)	926 (2)	3464 (1)	53 (1)
N₃	2508 (3)	4719 (2)	3419 (1)	53 (1)
N₄	731 (3)	4754 (2)	3995 (2)	35 (1)
C₁	502 (3)	2812 (3)	2825 (2)	35 (1)
C₂	−244 (4)	2817 (4)	2217 (2)	54 (1)
C₃	2670 (4)	1763 (3)	5076 (2)	36 (1)
C₄	3590 (4)	1388 (4)	5559 (2)	54 (2)
C₅	3594 (3)	3846 (3)	4847 (2)	38 (1)
C₆	4008 (4)	4268 (4)	5451 (2)	59 (2)
C₁₁	1113 (4)	38 (3)	4197 (2)	40 (1)
C₁₂	418 (4)	−641 (3)	4318 (2)	52 (2)
C₁₃	−684 (4)	−459 (3)	4222 (2)	55 (2)
C₁₄	−1064 (4)	410 (3)	4019 (2)	55 (2)
C₁₅	−331 (4)	1073 (3)	3903 (2)	40 (1)
C₂₁	3704 (3)	918 (3)	3637 (2)	41 (1)
C₂₂	4313 (4)	311 (3)	3388 (2)	52 (2)
C₂₃	3799 (4)	−308 (3)	2969 (2)	60 (2)
C₂₄	2673 (5)	−305 (3)	2787 (2)	58 (2)
C₂₅	2077 (4)	318 (3)	3034 (2)	43 (1)
C₃₁	1932 (4)	5338 (3)	3020 (2)	44 (1)
C₃₂	2452 (4)	5919 (3)	2707 (2)	53 (2)
C₃₃	3579 (4)	5869 (4)	2786 (2)	58 (2)
C₃₄	4155 (4)	5232 (3)	3180 (2)	51 (2)
C₃₅	3619 (3)	4671 (3)	3493 (2)	38 (1)
C₄₁	−351 (4)	4569 (3)	3894 (2)	46 (1)
C₄₂	−1077 (4)	5180 (4)	4052 (3)	65 (2)
C₄₃	−711 (4)	6004 (4)	4320 (3)	69 (2)
C₄₄	389 (4)	6206 (3)	4425 (2)	63 (2)
C₄₅	1091 (4)	5570 (3)	4263 (2)	47 (1)
	Anion			
P	3263 (1)	−2099 (1)	1458 (1)	48 (1)
F₁	4059 (3)	−2173 (2)	2097 (1)	78 (1)
F₂	4265 (3)	−2070 (3)	1174 (2)	103 (2)
F₃	2430 (3)	−2025 (3)	836 (1)	91 (1)
F₄	2242 (2)	−2120 (2)	1755 (1)	75 (1)
F₅	3227 (3)	−3204 (2)	1416 (2)	88 (1)
F₆	3286 (3)	−989 (2)	1529 (2)	86 (1)
	Molecule 1 of Crystallization			
Cl₁	3759 (2)	8993 (1)	4951 (1)	99 (1)
Cl₂	3068 (2)	7577 (2)	4061 (1)	118 (1)
C₇	3567 (5)	7797 (4)	4799 (3)	75 (2)
	Molecule 2 of Crystallization			
Cl₃	2626 (2)	3616 (1)	2025 (1)	112 (1)
Cl₄	3293 (3)	1737 (2)	1924 (1)	144 (1)
C₈	3307 (5)	2655 (4)	2369 (2)	77 (2)

[a] The numbers in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1 and 2. [c] This is one-third of the trace of the orthogonalized $\mathbf{B}_{ij}$ tensor.

anions (supplementary Figure S3), and CH₂Cl₂ and disordered H₂O solvent molecules of crystallization (supplementary Figure S4). Final atomic coordinates for nonhydrogen atoms of [3]⁺ and [4]²⁺ are listed with estimated standard deviations in Tables I and II, respectively. Anisotropic thermal parameters for non-hydrogen atoms of [3]⁺ and [4]²⁺ are given in supplementary Tables SI and SII; atomic coordinates for hydrogen atoms are given in supplementary Tables SIII and SIV. Bond lengths and angles for the cations [3]⁺ and [4]²⁺ are given with standard deviations in Tables

III–VI. Bond lengths and angles for the [PF₆]⁻ anions and CH₂Cl₂ solvent molecules of crystallization in [3]⁺ and [4]²⁺ are given in supplementary Tables SV–SVII. The structural parameters for the intramolecular hydrogen-bonding interactions in [3]⁺ are given in Table VII.

[(py)₅Co₃(OAc)₃(OH)₂][PF₆]₂. Although the dinuclear [(py)₄Co₂(OAc)₃(OH)₂]⁺ cation [3]⁺ possesses no rigorous crystallographic symmetry in the solid state, it approximates rather closely C_2 site symmetry with the idealized 2-fold axis passing through carbon atoms C₁ and C₂ and the midpoint of the Co₁→Co₂ vector. Both Co(III) ions are octahedrally coordinated to two pyridine nitrogen atoms, two bridging hydroxyl groups, an oxygen atom of a monodentate acetate anion, and an oxygen atom of a bridging bidentate acetate anion. The average Co–N distance is 1.957 (3, 9, 15, 4) Å,[9] and the average hydroxyl Co–O distance is 1.890 (3, 3, 5, 4) Å.[9] The Co–O distances to the monodentate and bridging bidentate acetate ligands average 1.891 (3, 1, 1, 2)[9] and 1.915 (2, 2, 2, 2) Å,[9] respectively. The dimer is composed of two octahedra sharing two common cis coordination sites that are occupied by the bridging hydroxyl oxygen atoms. As a result of both Co(III) ions also being coordinated to oxygens on the same "small-bite" bidentate acetate ligand, these octahedra are tipped toward each other, resulting in an 18° folding of the normally planar N₂CoO₂CoN₂ fused basal plane groupling along the O_{b1}→O_{b2} edge.

It is also of interest to note that the uncomplexed oxygen atoms of the monodentate acetate ligands each form an intramolecular hydrogen bond with one of the bridging hydroxyl groups. The structural parameters associated with these interactions are given in Table VII. These intramolecular hydrogen bonds undoubtedly help to stabilize the observed structure for this dimer and may also play an important role in the interconversion of cluster species in solution.

[(py)₅Co₃O(OAc)₃(OH)₂][PF₆]₂. The [(py)₅Co₃O(OAc)₃-(OH)₂]²⁺ cation (Figure 2) is a member of the familiar oxygen-centered three-metal carboxylate cluster series[10] and is composed of three octahedral Co(III) centers sharing common vertices: all three are bonded to a central O²⁻ atom (O_x) and Co₁ is bonded to the oxygen atoms of two hydroxyl groups that bridge to Co₂ and Co₃, respectively. The cation contains three bidentate acetate anions that bridge pairs of Co atoms and span the edges of the three Co triangle. Co₁ is bonded to the nitrogen of a single pyridine ligand while Co₂ and Co₃ are each bonded to the nitrogen atoms of two pyridine ligands. One pyridine nitrogen on each metal occupies a coordination site trans to the common μ_3-oxo atom.

Although the [(py)₅Co₃O(OAc)₃(OH)₂]²⁺ cation possesses no rigorous crystallographic symmetry in the solid state, it approximates rather closely C_{s-m} symmetry with the pseudo-mirror plane containing O_x, Co₁ and its σ-bonded pyridine, C₅, and C₆ and bisecting the Co₂→Co₃ vector. The 11 atoms or points (Co₁, O, N₁, C₁₁, C₁₂, C₁₃, C₁₄, C₁₅, C₅, C₆, and the midpoint of the Co₂→Co₃ vector) used to determine the reference plane are coplanar to within 0.02 Å. The three Co atoms describe an isosceles triangle with the Co₁⋯Co₂ and Co₁⋯Co₃ edges averaging 2.786 (1, 6, 6, 2) Å and the Co₂⋯Co₃ edge being 3.320 (1) Å. The central O_x atom is displaced by 0.71 Å below the least-squares mean plane of the three Co atoms while N₁, N₂, and N₃ are displaced 0.96, 0.70, and 0.72 Å, respectively, above this plane. The marked displacements of these atoms from the three Co mean plane and the dissimilar Co⋯Co distances are a result of the two single-atom hydroxyl bridges between Co₁ and the other cobalts and the presence of only one (bidentate acetate) bridge between Co₂ and Co₃. When all three metals are bridged by two bidentate ligands having similar "bites", the central oxygen atom and three

(9) The first number in parentheses following an average value of a bond length is the root-mean-square estimated standard deviation of an individual datum. The second and third numbers, when given, are the average and maximum deviations from the averaged value, respectively. The fourth number represents the number of individual measurements that are included in the average value.

(10) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*; Wiley: New York, 1980; p 154.

Table II. Atomic Coordinates for Non-Hydrogen Atoms in Crystalline $[Co_3(O)(OH)_2(NC_5H_5)_5(O_2CCH_3)_3][PF_6]_2 \cdot CH_2Cl \cdot H_2O^a$

atom type[b]	fractional coordinates			equiv isotropic thermal param, B, Å^2 × 10^c	atom type[b]	fractional coordinates			equiv isotropic thermal param, B, Å^2 × 10^c
	10^4x	10^4y	10^4z			10^4x	10^4y	10^4z	
				Cation					
Co$_1$	−1436 (1)	2327 (1)	1922 (1)	28 (1)	C$_{12}$	−3910 (4)	2162 (4)	2156 (4)	57 (2)
Co$_2$	−85 (1)	1396 (1)	1831 (1)	29 (1)	C$_{13}$	−3789 (4)	1893 (4)	2916 (4)	54 (2)
Co$_3$	6 (1)	3250 (1)	2407 (1)	29 (1)	C$_{14}$	−2992 (4)	1754 (4)	3376 (4)	47 (2)
O$_x$	−393 (2)	2449 (2)	1678 (2)	28 (1)	C$_{15}$	−2331 (3)	1883 (3)	3046 (3)	37 (2)
O$_1$	−947 (2)	1382 (2)	2368 (2)	33 (1)	C$_{21}$	182 (4)	−193 (4)	1319 (4)	43 (2)
O$_2$	−893 (2)	2929 (2)	2830 (2)	29 (1)	C$_{22}$	302 (4)	−993 (4)	1380 (4)	53 (2)
O$_3$	−1977 (2)	1828 (2)	941 (2)	36 (1)	C$_{23}$	328 (4)	−1333 (4)	2103 (5)	62 (3)
O$_4$	−829 (2)	1191 (2)	801 (2)	33 (1)	C$_{24}$	240 (4)	−904 (4)	2721 (5)	59 (3)
O$_5$	−1924 (2)	3260 (2)	1411 (2)	35 (1)	C$_{25}$	127 (4)	−114 (4)	2621 (4)	47 (2)
O$_6$	−722 (2)	3959 (2)	1708 (2)	35 (1)	C$_{31}$	400 (4)	4883 (3)	2915 (4)	40 (2)
O$_7$	685 (2)	1432 (2)	2852 (2)	33 (1)	C$_{32}$	613 (4)	5495 (4)	3426 (4)	46 (2)
O$_8$	786 (2)	2692 (2)	3219 (2)	36 (1)	C$_{33}$	754 (4)	5364 (4)	4237 (4)	52 (2)
N$_1$	−2435 (3)	2152 (3)	2308 (3)	32 (1)	C$_{34}$	667 (4)	4622 (4)	4499 (4)	49 (2)
N$_2$	95 (3)	252 (3)	1933 (3)	36 (1)	C$_{35}$	444 (3)	4032 (4)	3946 (3)	38 (2)
N$_3$	313 (3)	4147 (3)	3158 (3)	34 (1)	C$_{41}$	691 (4)	1907 (4)	638 (4)	38 (2)
N$_4$	825 (3)	1531 (3)	1340 (3)	33 (1)	C$_{42}$	1324 (4)	2006 (4)	268 (4)	55 (2)
N$_5$	879 (3)	3539 (3)	1891 (3)	37 (1)	C$_{43}$	2116 (4)	1730 (5)	621 (4)	73 (3)
C$_1$	−1591 (3)	1407 (3)	560 (3)	34 (2)	C$_{44}$	2256 (4)	1352 (5)	1337 (4)	72 (3)
C$_2$	−2074 (4)	1143 (4)	−253 (3)	51 (2)	C$_{45}$	1607 (4)	1251 (4)	1688 (4)	50 (2)
C$_3$	−1500 (4)	3861 (3)	1366 (3)	36 (2)	C$_{51}$	677 (4)	3764 (4)	1131 (4)	45 (2)
C$_4$	−1946 (4)	4525 (4)	869 (4)	52 (2)	C$_{52}$	1285 (5)	3985 (5)	748 (5)	65 (3)
C$_5$	952 (3)	1967 (3)	3331 (3)	33 (2)	C$_{53}$	2094 (5)	3972 (5)	1156 (6)	87 (4)
C$_6$	1526 (4)	1762 (4)	4138 (3)	45 (2)	C$_{54}$	2312 (5)	3749 (7)	1933 (6)	110 (4)
C$_{11}$	−3218 (3)	2291 (4)	1865 (4)	45 (2)	C$_{55}$	1690 (4)	3542 (5)	2292 (4)	73 (3)
				Anion 1					
P$_1$	4358 (1)	2738 (1)	132 (1)	51 (1)	F$_{14}$	4140 (3)	2491 (3)	930 (2)	74 (2)
F$_{11}$	5041 (3)	3327 (3)	615 (2)	77 (2)	F$_{15}$	3653 (3)	3376 (3)	−30 (3)	82 (2)
F$_{12}$	4578 (2)	2981 (3)	−681 (2)	63 (1)	F$_{16}$	5069 (3)	2072 (3)	283 (2)	79 (2)
F$_{13}$	3695 (3)	2128 (3)	−362 (2)	78 (2)					
				Anion 2					
P$_2$	1057 (1)	6558 (1)	1239 (1)	50 (1)	F$_{24}$	300 (3)	7124 (3)	879 (3)	99 (2)
F$_{21}$	1673 (4)	7253 (3)	1443 (4)	124 (3)	F$_{25}$	1213 (3)	6453 (4)	416 (3)	132 (3)
F$_{22}$	1791 (3)	6002 (4)	1604 (4)	131 (3)	F$_{26}$	884 (3)	6698 (3)	2077 (3)	99 (2)
F$_{23}$	421 (4)	5875 (3)	1072 (4)	139 (3)					
				Solvent of Crystallization					
Cl$_1$	6856 (2)	89 (2)	1903 (2)	146 (2)	C$_{s1}$	7273 (7)	−797 (5)	1792 (6)	114 (5)
Cl$_2$	8015 (2)	−745 (2)	1303 (3)	168 (2)					
				Disordered Solvent^d					
O$_{s1}$	5928 (7)	4982 (7)	907 (8)	102 (5)	O$_{s2}$	5632 (10)	4911 (7)	−36 (11)	146 (8)

^{a}The numbers in parentheses are the estimated standard deviations in the last significant digit. ^{b}Atoms are labeled in agreement with Figures 4–6. ^{c}This is one-third of the trace of the orthogonalized B_{ij} tensor. ^{d}Electron density at positions corresponding to O$_{s1}$ and O$_{s2}$ appears to result from disordered solvent molecules (presumably water); anisotropic oxygen atoms with occupancies of 0.50 were included at these sites in the structural model.

metals tend to be more coplanar.

The non-hydrogen atoms of all five pyridine ligands are coplanar to within 0.008 Å, and the maximum displacement of a σ-bonded Co from its respective pyridine least-squares mean plane is 0.02 Å. The non-hydrogen atoms of each acetate anion are coplanar to within 0.004 Å, but one σ-bonded cobalt for each is displaced by 0.19–0.24 Å.

The average oxo, acetate, and hydroxyl Co–O bond lengths are 1.875 (3, 11, 17, 3),[9] 1.897 (3, 6, 15, 6),[9] and 1.895 (4, 8, 15, 4) Å,[9] respectively, while the average pyridine Co–N bond length is 1.963 (5, 18, 34, 5) Å.[9]

Discussion

The fact that these cluster complexes are prepared in the presence of a peracid is of interest in studies of autoxidation reactions. Peracids formed from the reaction of aldehydes with oxygen are present in autoxidation reactions and are presumed to play a major role in the regeneration of the cobalt catalyst in catalyzed autoxidations.[11] Under favorable conditions, i.e. low bromide concentration, [5]$^+$ can be prepared in large quantities by using air and xylene as the oxidizing agent in place of peracetic

acid. In this case, the actual oxidant is presumably pertoluic acid, which is formed in situ since toluic acid is formed as a coproduct. The fact that [5]$^+$ reacts with water to produce a mixture of [3]$^+$ and [4]$^{2+}$ is pertinent in light of the observation by Jones of three separate cobalt(III) complexes in acetic acid solution, since all autoxidation reactions produce water. The analogy between this system and that without pyridine becomes clear when one considers the similarity of [3]$^+$, [4]$^{2+}$, and [5]$^+$ to the structures previously proposed for cobaltic acetate and the suggestion that at least two of the pyridine-free cobaltic acetates are in equilibrium.[6] In the system described here, three cobalt clusters can be simultaneously present in solution and their relative concentrations are dependent mainly upon the amount of water in the solvent. For example, [5][PF$_6$] can be isolated in pure form from a solvent composition of 80% acetic acid and 20% water, whereas from 50% aqueous acetic acid were isolated [3][PF$_6$], [4][PF$_6$]$_2$, and [5][PF$_6$]$_2$. In 90% water, only [3][PF$_6$] and [4][PF$_6$]$_2$ were isolated; however, from glacial acetic acid were isolated only [5][PF$_6$] and [6][PF$_6$]. At this point, it is unknown if [3]$^+$ and [4]$^{2+}$ are directly interconvertable or whether [5]$^+$ is involved as an intermediate.

The mechanism by which [5]$^+$ is converted to [3]$^+$ and [4]$^{2+}$ may involve the stepwise interchange of ligands and cleavage of the oxo-centered framework or the complete disassembly of the cluster into intermediate monomeric species. The oxo-centered

(11) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic: New York, 1981.

Table III. Bond Lengths (Å) Involving the $[Co_2(OH)_2(O_2CCH_3)_3(NC_5H_5)_4]^+$ Cation in Crystalline $[Co_2(OH)_2(O_2CCH_3)_3(NC_5H_5)_4][PF_6]\cdot2CH_2Cl_2{}^{a,b}$

Co_1-Co_2	2.811 (1)		
Co_1-O_{b1}	1.893 (3)	Co_1-O_{b2}	1.885 (3)
Co_2-O_{b1}	1.891 (3)	Co_2-O_{b2}	1.891 (3)
Co_1-O_1	1.916 (2)	Co_2-O_2	1.913 (2)
Co_1-O_3	1.892 (3)	Co_2-O_5	1.890 (2)
Co_1-N_1	1.942 (3)	Co_2-N_3	1.961 (3)
Co_1-N_2	1.970 (3)	Co_2-N_4	1.954 (3)
$O_{b1}-H_{b1}$	0.94 (4)	$O_{b2}-H_{b2}$	0.82 (4)
O_1-C_1	1.258 (5)		
O_2-C_1	1.266 (5)		
O_3-C_3	1.288 (5)	O_5-C_5	1.289 (5)
O_4-C_3	1.219 (6)	O_6-C_5	1.233 (5)
N_1-C_{11}	1.343 (5)	N_3-C_{31}	1.353 (5)
N_1-C_{15}	1.339 (5)	N_3-C_{35}	1.357 (5)
N_2-C_{21}	1.354 (5)	N_4-C_{41}	1.339 (6)
N_2-C_{25}	1.361 (5)	N_4-C_{45}	1.343 (5)
C_1-C_2	1.496 (5)		
C_3-C_4	1.499 (6)		
C_5-C_6	1.500 (6)		
$C_{11}-C_{12}$	1.372 (7)	$C_{31}-C_{32}$	1.365 (7)
$C_{12}-C_{13}$	1.364 (7)	$C_{32}-C_{33}$	1.375 (7)
$C_{13}-C_{14}$	1.366 (7)	$C_{33}-C_{34}$	1.365 (6)
$C_{14}-C_{15}$	1.384 (7)	$C_{34}-C_{35}$	1.361 (7)
$C_{21}-C_{22}$	1.367 (7)	$C_{41}-C_{42}$	1.369 (8)
$C_{22}-C_{23}$	1.355 (7)	$C_{42}-C_{43}$	1.354 (7)
$C_{23}-C_{24}$	1.366 (8)	$C_{43}-C_{44}$	1.365 (7)
$C_{24}-C_{25}$	1.369 (8)	$C_{44}-C_{45}$	1.374 (7)

^{a} The numbers in parentheses are the estimated standard deviations in the last significant digit. ^{b} Atoms are labeled in agreement with Figure 1.

Table IV. Bond Angles (deg) Involving the $[Co_2(OH)_2(O_2CCH_3)_3(NC_5H_5)_4]^+$ Cation in Crystalline $[Co_2(OH)_2(O_2CCH_3)_3(NC_5H_5)_4][PF_6]\cdot2CH_2Cl_2{}^{a,b}$

$Co_2Co_1O_{b1}$	42.0 (1)	$Co_1Co_2O_{b1}$	42.1 (1)
$Co_2Co_1O_{b2}$	42.0 (1)	$Co_1Co_2O_{b2}$	41.8 (1)
$Co_2Co_1O_1$	81.8 (1)	$Co_1Co_2O_2$	81.4 (1)
$Co_2Co_1O_3$	103.2 (1)	$Co_1Co_2O_5$	103.9 (1)
$Co_2Co_1N_1$	134.0 (1)	$Co_1Co_2N_3$	131.1 (1)
$Co_2Co_1N_2$	131.1 (1)	$Co_1Co_2N_4$	133.2 (1)
$O_{b1}Co_1O_{b2}$	82.9 (1)	$O_{b1}Co_2O_{b2}$	82.8 (1)
$O_{b1}Co_1O_1$	89.4 (1)	$O_{b1}Co_2O_2$	88.1 (1)
$O_{b1}Co_1O_3$	96.4 (1)	$O_{b1}Co_2O_5$	93.5 (1)
$O_{b1}Co_1N_1$	93.1 (1)	$O_{b1}Co_2N_3$	172.1 (1)
$O_{b1}Co_1N_2$	173.0 (1)	$O_{b1}Co_2N_4$	92.1 (1)
$O_{b2}Co_1O_1$	89.4 (1)	$O_{b2}Co_2O_2$	90.1 (1)
$O_{b2}Co_1O_3$	92.4 (1)	$O_{b2}Co_2O_5$	96.2 (1)
$O_{b2}Co_1N_1$	175.9 (1)	$O_{b2}Co_2N_3$	91.4 (1)
$O_{b2}Co_1N_2$	90.5 (1)	$O_{b2}Co_2N_4$	174.9 (1)
$O_1Co_1O_3$	174.1 (1)	$O_2Co_2O_5$	173.6 (1)
$O_1Co_1N_1$	89.5 (1)	$O_2Co_2N_3$	86.7 (1)
$O_3Co_1N_1$	89.1 (1)	$O_5Co_2N_3$	92.4 (1)
$O_1Co_1N_2$	88.2 (1)	$O_2Co_2N_4$	89.5 (1)
$O_3Co_1N_2$	86.1 (1)	$O_5Co_2N_4$	84.2 (1)
$N_1Co_1N_2$	93.4 (1)	$N_3Co_2N_4$	93.7 (1)
$Co_1O_{b1}Co_2$	95.9 (1)	$Co_1O_{b2}Co_2$	96.2 (1)
$Co_1O_{b1}H_{b1}$	105 (2)	$Co_1O_{b2}H_{b2}$	112 (3)
$Co_2O_{b1}H_{b1}$	119 (2)	$Co_2O_{b2}H_{b2}$	99 (3)
$Co_1O_1C_1$	125.0 (2)	$Co_1O_3C_3$	127.6 (2)
$Co_2O_2C_1$	125.4 (2)	$Co_2O_5C_5$	130.3 (3)
$Co_1N_1C_{11}$	121.2 (3)	$Co_2N_3C_{31}$	121.0 (3)
$Co_1N_1C_{15}$	120.7 (3)	$Co_2N_3C_{35}$	120.1 (3)
$C_{11}N_1C_{15}$	118.0 (4)	$C_{31}N_3C_{35}$	118.5 (4)
$Co_1N_2C_{21}$	119.4 (3)	$Co_2N_4C_{41}$	120.5 (3)
$Co_1N_2C_{25}$	122.0 (3)	$Co_2N_4C_{45}$	121.8 (3)
$C_{21}N_2C_{25}$	118.6 (4)	$C_{41}N_4C_{45}$	117.6 (4)
$O_1C_1O_2$	126.3 (3)		
$O_1C_1C_2$	117.3 (4)		
$O_2C_1C_2$	116.4 (4)		
$O_3C_3O_4$	125.3 (3)	$O_5C_5O_6$	125.3 (4)
$O_3C_3C_4$	113.8 (4)	$O_5C_5C_6$	114.0 (4)
$O_4C_3C_4$	120.9 (4)	$O_6C_5C_6$	120.8 (4)
$N_1C_{11}C_{12}$	122.3 (4)	$N_3C_{31}C_{32}$	121.3 (4)
$C_{11}C_{12}C_{13}$	119.6 (4)	$C_{31}C_{32}C_{33}$	119.9 (4)
$C_{12}C_{13}C_{14}$	118.7 (5)	$C_{32}C_{33}C_{34}$	118.7 (5)
$C_{13}C_{14}C_{15}$	119.6 (4)	$C_{33}C_{34}C_{35}$	120.2 (5)
$C_{14}C_{15}N_1$	121.8 (4)	$C_{34}C_{35}N_3$	121.4 (4)
$N_2C_{21}C_{22}$	121.1 (4)	$N_4C_{41}C_{42}$	122.1 (4)
$C_{21}C_{22}C_{23}$	120.0 (5)	$C_{41}C_{42}C_{43}$	120.1 (5)
$C_{22}C_{23}C_{24}$	119.6 (5)	$C_{42}C_{43}C_{44}$	118.5 (5)
$C_{23}C_{24}C_{25}$	119.7 (5)	$C_{43}C_{44}C_{45}$	119.5 (4)
$C_{24}C_{25}N_2$	120.9 (4)	$C_{44}C_{45}N_4$	122.1 (4)

^{a} The numbers in parentheses are the estimated standard deviations in the last significant digit. ^{b} Atoms are labeled in agreement with Figure 1.

framework appears to remain intact for most ligand substitutions. For example, the acetate ligands are labile at 70 °C, as evidenced by the exchange with deuteriated ligands at this temperature, and they can be easily replaced by other carboxylate groups as described above. The oxo-centered framework remains intact for other substitutions as well, such as the displacement of one acetate ligand for an alkoxide. Cluster complexes similar to $[5]^+$ where the bridging hydroxyl ligand has been replaced by a bridging alkoxy group can be prepared by heating [5][PF_6] and [6][PF_6] in acetonitrile containing 10% by volume of a primary alcohol. Several cluster complexes resulting from such a displacement have been prepared and will be discussed in a separate paper. Thus, it is conceivable that $[4]^{2+}$ can be formed without the disruption of the cluster framework; however, it is obvious that the formation of $[3]^+$ is more complicated.

These results indicate that the actual cobaltic acetate species present in an autoxidation mixture may be a function of the solvent medium, and may also help to explain the complex kinetics observed for these type of reactions.[12] The isolation of the pyridine-substituted cobaltic acetates described here and the observation that they are interconvertible with the previously described oxo-centered cluster $[5]^+$ is consistent with the dynamic behavior of cobaltic acetates described by Jones. The conversion of an oxo-centered trinuclear cluster to a dinuclear cluster has, to our knowledge, not been previously reported and may be of general scope.

Experimental Section

Peracetic Acid Preparation of $[(py)_4Co_2(OAc)_3(OH)_2][PF_6]$, $[3][PF_6]$, **and** $[(py)_5Co_3(OAc)_3(OH)_2][PF_6]_2$, $[4][PF_6]_2$. To a 250 mL, three-necked flask equipped with a reflux condenser, dropping funnel, thermometer, spin bar, heating mantle, and safety shield were added cobaltous acetate

(6.0 g; 24 mmol), pyridine (4.0 g; 51 mmol), water (50 mL), and acetic acid (10 mL). The mixture was stirred, and peracetic acid (8.4 g of 35% acetic acid solution; 37 mmol) was added dropwise. The temperature of the mixture rose from 28 to 35 °C during the addition of the peracetic acid, and the color of the mixture changed from violet to purple. The mixture was slowly heated to reflux and refluxed for 10 min. The color changed from purple to brown. The heat was removed, NH_4PF_6 (2.5 g; 15 mmol) dissolved in 20 mL of water was added, and the mixture was allowed to cool to room temperature and then chilled in an ice bath. The product mixture was collected by filtration, washed with water, and triturated with methylene chloride. The remaining residue $[4][PF_6]_2$ was recrystallized from acetonitrile/ether to give 3.0 g of dark brown crystals (31%). The methylene chloride washings were combined and transferred to a separatory funnel, where the water was separated. The solution was dried (MgSO_4), and the volume was adjusted to 60 mL with methylene chloride. The solution was layered with 100 mL of petroleum ether, which caused the product to crystallize as large, purple crystals after the mixture had been allowed to stand overnight. The yield was 3.9 g (34%).

^{1}H NMR spectrum of [3][PF_6] (400 MHz; CD_2Cl_2: δ 8.3 (d, 8 H), 8.0 (t, 4 H), 7.5 (t, 8 H), 7.4 (s, 2 H), 2.3 (s, 3 H), 2.1 (s, 6 H). The

(12) (a) Kashima, M.; Kamiya, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 481. (b) Hanotier, J.; Hanotier-Bridoux, M. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1035. (c) Scott, E. J. Y.; Chester, A. W. *J. Phys. Chem.* **1972**, *76*, 1520. (d) Morimoto, T.; Ogata, Y. *J. Chem. Soc. B* **1967**, 1353.

Table V. Bond Lengths Involving the $[Co_3(O)(OH)_2(NC_5H_5)_5(O_2CCH_3)_3]^{2+}$ Cation in Crystalline $[Co_3(O)(OH)_2(NC_5H_5)_5(O_2CCH_3)_3][PF_6]_2 \cdot CH_2Cl_2 \cdot H_2O^{a,b}$

$Co_1 \cdots Co_2$	2.780 (1)	N_1-C_{11}	1.335 (6)
$Co_1 \cdots Co_3$	2.791 (1)	N_1-C_{15}	1.328 (7)
$Co_2 \cdots Co_3$	3.320 (1)	$C_{11}-C_{12}$	1.384 (9)
		$C_{12}-C_{13}$	1.361 (10)
Co_1-O_x	1.892 (4)	$C_{13}-C_{14}$	1.362 (8)
Co_2-O_x	1.872 (3)	$C_{14}-C_{15}$	1.379 (9)
Co_3-O_x	1.862 (3)		
		N_2-C_{21}	1.349 (8)
Co_1-O_1	1.880 (4)	N_2-C_{25}	1.337 (8)
Co_1-O_2	1.894 (4)	$C_{21}-C_{22}$	1.384 (9)
		$C_{22}-C_{23}$	1.373 (11)
Co_2-O_1	1.899 (4)	$C_{23}-C_{24}$	1.340 (12)
Co_3-O_2	1.906 (4)	$C_{24}-C_{25}$	1.370 (9)
Co_1-N_1	1.962 (5)		
Co_2-N_2	1.983 (5)	N_3-C_{31}	1.350 (7)
Co_2-N_4	1.929 (5)	N_3-C_{35}	1.341 (7)
Co_3-N_3	1.990 (4)	$C_{31}-C_{32}$	1.357 (9)
Co_3-N_5	1.953 (5)	$C_{32}-C_{33}$	1.382 (10)
		$C_{33}-C_{34}$	1.370 (10)
Co_1-O_3	1.900 (3)	$C_{34}-C_{35}$	1.374 (9)
Co_1-O_5	1.898 (4)		
		N_4-C_{41}	1.342 (7)
Co_2-O_4	1.909 (3)	N_4-C_{45}	1.357 (7)
Co_2-O_7	1.882 (3)	$C_{41}-C_{42}$	1.377 (10)
		$C_{42}-C_{43}$	1.368 (9)
Co_3-O_6	1.898 (4)	$C_{43}-C_{44}$	1.364 (11)
Co_3-O_8	1.892 (3)	$C_{44}-C_{45}$	1.378 (10)
O_3-C_1	1.259 (7)		
O_4-C_1	1.269 (6)	N_5-C_{51}	1.328 (8)
		N_5-C_{55}	1.332 (7)
O_5-C_3	1.260 (7)	$C_{51}-C_{52}$	1.395 (12)
O_6-C_3	1.271 (6)	$C_{52}-C_{53}$	1.332 (11)
		$C_{53}-C_{54}$	1.355 (14)
O_7-C_5	1.236 (6)	$C_{54}-C_{55}$	1.383 (13)
O_8-C_5	1.275 (7)		
		O_1-H_{O1}	0.64 (3)
C_1-C_2	1.492 (7)	O_2-H_{O2}	0.79 (4)
C_3-C_4	1.495 (8)		
C_5-C_6	1.506 (7)		

a The numbers in parentheses are the estimated standard deviations in the last significant digit. *b* Atoms are labeled in agreement with Figure 4.

Table VI. Bond Angles Involving the $[Co_3(O)(OH)_2(NC_5H_5)_5(O_2CCH_3)_3]^{2+}$ Cation Non-Hydrogen Atoms in Crystalline $[Co_3(O)(OH)_2(NC_5H_5)_5(O_2CCH_3)_3][PF_6]_2 \cdot CH_2Cl_2 \cdot H_2O^{a,b}$

$O_xCo_1O_1$	82.6 (2)	$O_2Co_1N_1$	93.0 (2)
$O_xCo_1O_2$	82.6 (2)	$O_3Co_1O_5$	85.5 (2)
$O_xCo_1O_3$	94.8 (2)	$O_3Co_1N_1$	90.2 (2)
$O_xCo_1O_5$	95.7 (2)	$O_5Co_1N_1$	89.9 (2)
$O_1Co_1O_2$	94.1 (2)	$O_xCo_1N_1$	172.7 (2)
$O_1Co_1O_3$	91.5 (2)	$O_1Co_1O_5$	176.5 (2)
$O_1Co_1N_1$	92.0 (2)	$O_2Co_1O_3$	173.4 (2)
$O_2Co_1O_5$	88.7 (2)		
$O_xCo_2O_1$	82.6 (2)	$O_xCo_3O_2$	83.1 (2)
$O_xCo_2O_4$	87.9 (1)	$O_xCo_3O_6$	89.4 (1)
$O_xCo_2O_7$	101.0 (1)	$O_xCo_3O_8$	100.3 (2)
$O_xCo_2N_4$	92.0 (2)	$O_xCo_3N_5$	92.6 (2)
$O_1Co_2O_4$	94.5 (2)	$O_2Co_3O_6$	90.4 (2)
$O_1Co_2O_7$	86.7 (2)	$O_2Co_3O_8$	90.6 (2)
$O_1Co_2N_2$	93.3 (2)	$O_2Co_3N_3$	93.3 (2)
$O_4Co_2N_2$	86.8 (2)	$O_6Co_3N_3$	86.0 (2)
$O_4Co_2N_4$	89.4 (2)	$O_6Co_3N_5$	87.8 (2)
$O_7Co_2N_2$	84.3 (2)	$O_8Co_3N_3$	84.2 (2)
$O_7Co_2N_4$	90.3 (2)	$O_8Co_3N_5$	91.9 (2)
$N_2Co_2N_4$	92.4 (2)	$N_3Co_3N_5$	90.9 (2)
$O_xCo_2N_2$	173.0 (2)	$O_xCo_3N_3$	174.2 (2)
$O_1Co_2N_4$	173.2 (2)	$O_2Co_3N_5$	175.3 (2)
$O_4Co_2O_7$	171.1 (2)	$O_6Co_3O_8$	170.3 (2)
$Co_1O_xCo_2$	95.2 (2))	$Co_1O_1Co_2$	94.7 (2)
$Co_1O_xCo_3$	96.1 (2)	$Co_1O_2Co_3$	94.5 (2)
$Co_2O_xCo_3$	125.5 (2)		
$Co_1O_3C_1$	123.1 (3)	$Co_1O_1H_{O1}$	112 (3)
$Co_1O_5C_3$	123.0 (3)	$Co_2O_1H_{O1}$	109 (3)
$Co_2O_4C_1$	125.8 (4)	$Co_1O_2H_{O2}$	101 (3)
$Co_3O_6C_3$	126.8 (4)	$Co_3O_2H_{O2}$	112 (4)
$Co_2O_7C_5$	133.2 (3)		
$Co_3O_8C_5$	132.9 (3)		
$O_3C_1O_4$	126.2 (5)	$Co_1N_1C_{11}$	123.2 (4)
$O_3C_1C_2$	117.0 (5)	$Co_1N_1C_{15}$	118.7 (3)
$O_4C_1C_2$	116.9 (5)	$C_{11}N_1C_{15}$	118.1 (5)
$O_5C_3O_6$	125.9 (5)	$Co_2N_2C_{21}$	122.2 (4)
$O_5C_3C_4$	117.5 (5)	$Co_2N_2C_{25}$	120.8 (4)
$O_6C_3C_4$	116.6 (5)	$C_{21}N_2C_{25}$	117.0 (5)
$O_7C_5O_8$	126.7 (4)	$Co_3N_3C_{31}$	123.1 (4)
$O_7C_5C_6$	118.3 (5)	$Co_3N_3C_{35}$	119.9 (4)
$O_8C_5C_6$	115.1 (5)	$C_{31}N_3C_{35}$	117.0 (5)
		$Co_2N_4C_{41}$	120.1 (4)
$N_1C_{11}C_{12}$	121.8 (6)	$Co_2N_4C_{45}$	121.4 (4)
$C_{11}C_{12}C_{13}$	119.2 (5)	$C_{41}N_4C_{45}$	118.5 (5)
$C_{12}C_{13}C_{14}$	119.5 (7)	$Co_3N_5C_{51}$	120.8 (4)
$C_{13}C_{14}C_{15}$	118.4 (6)	$Co_3N_5C_{55}$	121.5 (5)
$C_{14}C_{15}N_1$	123.0 (5)	$C_{51}N_5C_{55}$	117.7 (6)
$N_2C_{21}C_{22}$	122.8 (6)	$N_3C_{31}C_{32}$	123.2 (6)
$C_{21}C_{22}C_{23}$	117.4 (7)	$C_{31}C_{32}C_{33}$	118.9 (6)
$C_{22}C_{23}C_{24}$	121.0 (7)	$C_{32}C_{33}C_{34}$	119.0 (6)
$C_{23}C_{24}C_{25}$	118.7 (7)	$C_{33}C_{34}C_{35}$	118.9 (6)
$C_{24}C_{25}N_2$	123.2 (7)	$C_{34}C_{35}N_3$	122.9 (6)
$N_4C_{41}C_{42}$	121.5 (5)	$N_5C_{51}C_{52}$	122.2 (6)
$C_{41}C_{42}C_{43}$	120.2 (7)	$C_{51}C_{52}C_{53}$	119.3 (8)
$C_{42}C_{43}C_{44}$	118.5 (7)	$C_{52}C_{53}C_{54}$	119.5 (9)
$C_{43}C_{44}C_{45}$	120.1 (6)	$C_{53}C_{54}C_{55}$	119.4 (7)
$C_{44}C_{45}N_4$	121.2 (6)	$C_{54}C_{55}N_5$	121.9 (7)

a The numbers in parentheses are the estimated standard deviations in the last significant digit. *b* Atoms are labeled in agreement with Figure 4.

fast atom bombardment (FAB) mass spectrum of **3** consisted of a parent ion at m/e 645 and fragment ions corresponding to loss of pyridine, acetate, and hydroxyl ligands. Anal. Calcd for $C_{26}H_{31}N_4Co_2F_6O_8P \cdot CH_2Cl_2$: C, 35.00; H, 3.65; N, 5.83; Co, 12.29; F, 11.88. Found: C, 35.50; H, 3.53; N, 6.05; Co, 12.6; F, 12.56.

^{1}H NMR spectrum of [**4**][PF$_6$]$_2$ (400 MHz; CD$_3$CN: δ 8.8 (d, 2 H), 8.4 (d, 4 H), 8.1 (m, 3 H), 7.9 (d, 4 H), 7.7 (m, 4 H), 7.6 (t, 4 H), 7.2 (t, 4 H), 5.7 (s, 2 H; CH$_2$Cl$_2$ of crystallization), 2.6 (s, 3 H), 2.2 (s, 6 H), 0.9 (br, 2 H; H$_2$O). The FAB mass spectrum of [**4**][PF$_6$]$_2$ contained a signal at m/e 945 corresponding to the dication combined with a PF$_6$ ion, followed by a complex pattern of signals. Anal. Calcd for $C_{31}H_{36}Co_3F_{12}N_5O_9P_2 \cdot CH_2Cl_2 \cdot H_2O$: C, 32.21; H, 3.36; N, 5.87; Co, 14.85; F, 19.13. Found: C, 32.73; H, 3.30; N, 5.93; Co, 14.8; F, 19.44.

Preparation of [(py)$_3$Co$_3$O(OAc)$_5$OH][PF$_6$]. To a 100-mL flask equipped with a heating mantle, thermometer, and spin bar were added cobaltous acetate (5.00 g; 20 mmol), acetic acid (50 mL), and pyridine (1.75 g; 22 mmol). The resulting mixture was warmed until all of the cobalt had dissolved, and peracetic acid (4.36 g of 35%; 20 mmol) was added slowly while the solution was vigorously stirred. The color of the solution turned dark brown. After the addition of peracetic acid was complete, water (12 mL) was added and the resulting solution was heated for 1 h at 82 °C and then allowed to cool to 70 °C. A solution of NH$_4$PF$_6$ (2.2 g) dissolved in water (7 mL) was added, and the resulting mixture was allowed to cool to room temperature. The product was collected by filtration and vacuum-dried. The yield was 4.8 g (81%). Anal. Calcd for $C_{25}H_{31}Co_3F_6N_3O_{12}P$: C, 33.82; H, 3.49; Co, 19.95; F, 13.08; N, 4.74. Found: C, 34.15; H, 3.56; Co, 18.2; F, 13.08; N, 4.87. ^{1}H NMR (400 MHz; CD$_2$Cl$_2$): δ 9.2 (d, 2 H), 8.8 (d, 4 H), 8.3 (t, 1 H), 8.1 (t, 2 H), 7.9 (t, 2 H), 7.7 (t, 4 H), 2.2 (s, 3 H), 2.1 (s, 6 H), 2.0 (s, 6 H). FAB mass spectrum (positive mode): m/e 742 (parent ion) followed by ions corresponding to the successive loss of pyridine and acetate ligands.

Reaction of [(py)$_3$Co$_3$O(OAc)$_5$OH]$^+$ with Water Containing Pyridine. [(py)$_3$Co$_3$O(OAc)$_5$OH][OAc] was prepared by the addition of peracetic acid (4.4 g of 35%) to an acetic acid solution (40 mL) of cobaltous acetate (5.0 g) and pyridine (1.6 g) at 70 °C followed by the evaporation of the solvent. To a 100-mL flask equipped with a heating mantle, reflux

condenser, and spin bar were added [(py)$_3$Co$_3$O(OAc)$_5$OH][OAc] (16.5 g; 20 mmol), pyridine (1.1 g; 13.5 mmol), and 40 mL of 50% aqueous acetic acid. The resulting solution was refluxed for 1 h. After cooling, NH$_4$PF$_6$ (1.6 g dissolved in 3 mL of water) was added and the solvent was evaporated. The residue was extracted with methylene chloride. The remaining material, which was insoluble in methylene chloride, was taken up in acetonitrile, and the mixture was filtered and evaporated to give 1.40 g (1.2 mmol) of pure [**4**][PF$_6$]$_2$, as determined by ^{1}H NMR and FAB mass spectroscopy. The methylene chloride solution was evaporated to give 5.96 g of residue. The ^{1}H NMR spectrum of the residue showed it to consist of a mixture of [**3**][PF$_6$], [**4**][PF$_6$]$_2$, and [**5**][PF$_6$] in a ratio

Table VII. Close Contacts Involving Hydrogen Atoms in Crystalline $[(py)_4Co_2(OAc)_3(OH)_2][PF_6]\cdot2CH_2Cl_2{}^a$

donor atom (D)[b]	acceptor atom (A)	D···A,[c] Å	H···A,[c] Å	H-D···A,[c] deg	D-H···A,[c] deg	H···A-X,[c,d] deg	asymmetric unit of A[e]
$O_{b1}-H_{b1}$	O_4	2.622 (4)	1.75 (4)	18 (3)	153 (3)	108 (3) (C_3)	x, y, z
$O_{b2}-H_{b2}$	O_6	2.656 (4)	1.86 (4)	10 (3)	166 (3)	102 (3) (C_5)	x, y, z

[a] Atoms are labeled in agreement with Figure 1. [b] The hydrogen atom involved in the interaction is also indicated. [c] The numbers in parentheses are the estimated standard deviations in the last significant digit. [d] The symbol X is used to denote the carbon atom that is covalently bonded to the acceptor oxygen atom. [e] All donor and acceptor atoms belong to the same asymmetric unit for which fractional atomic coordinates are given in Tables I and V.

of 19:11:4, respectively. The ratio was determined by comparison of the relative integration of the ortho hydrogens of the pyridine ligands. The total amount of [3][PF$_6$] was calculated to be 3.16 g (3.3 mmol), the amount of [4][PF$_6$]$_2$ was 3.66 g (3.1 mmol), and the amount of [5][PF$_6$]$_2$ was 0.69 g (0.6 mmol). Eight-nine percent of the starting cobalt was accounted for as cobalt(III). A 0.57-g amount of blue material was insoluble in methylene chloride and acetonitrile.

Reaction of [(py)$_3$Co$_3$O(OAc)$_5$OH]$^+$ with Water in the Absence of Pyridine. The above procedure was repeated except that the added pyridine was omitted. Extraction with methylene chloride left 0.90 g of [4][PF$_6$]$_2$ and 1.23 g of insoluble blue material. The methylene chloride extract produced 4.14 g of a mixture that was mainly [5][PF$_6$], along with a lesser amount of [3][PF$_6$] and minor amounts of several other compounds observed by ^{1}H NMR spectroscopy that did not lend themselves to ready identification.

Reaction of [3][PF$_6$] with Acetic Acid. To a 50-mL flask equipped with a reflux condenser, heating mantle, and spin bar were added [3][PF$_6$] (1.00 g; 1.04 mmol) and 20 mL of acetic acid. The resulting mixture was refluxed for 1 h and allowed to cool. The mixture was filtered, and 0.30 g of a brown solid was collected. The FAB mass spectrum and the ^{1}H NMR spectrum of the solid were consistent with the formula [(py)$_3$Co$_3$O(OAc)$_6$][PF$_6$]. Evaporation of the filtrate left 0.47 g of a brown residue, which was shown by FAB mass spectroscopy and ^{1}H NMR spectroscopy to be a mixture of [(py)$_3$Co$_3$O(OAc)$_6$][PF$_6$] and [(py)$_3$Co$_3$O(OAc)$_5$OH][PF$_6$]. The combined yield of the trinuclear clusters was 96%.

Reaction of [4][PF$_6$]$_2$ with Acetic Acid. To a 25-mL flask equipped with a reflux condenser, heating mantle, and spin bar were added [4]-[PF$_6$]$_2$ (1.00 g; 1.0 mmol) and 12 mL of acetic acid. The resulting mixture was refluxed for 15 min and allowed to cool. Filtration of the mixture produced 0.844 g (94%) of solid product, which consisted of a 3:1 mixture of [(py)$_3$Co$_3$O(OAc)$_5$OH][PF$_6$] and [(py)$_3$Co$_3$O(OAc)$_6$]-[PF$_6$], respectively, as determined by ^{1}H NMR spectroscopy.

Reaction of [5][PF$_6$] with CD$_3$CO$_2$D. To a 50-mL flask equipped with a heating mantle, thermometer, and spin bar were added [(py)$_3$Co$_3$O-(OAc)$_5$OH][PF$_6$] (1.00 g; 1.1 mmol) and 10 mL of acetic-d_3 acid-d. The resulting mixture was heated at 70 °C for 30 min and allowed to cool. The product was collected by filtration, washed with ether, and dried under vacuum. The yield was 0.95 g. The FAB mass spectrum displayed a molecular ion at m/e 802, followed by ions consistent with the loss of pyridine and CD$_3$CO$_2$, indicating complete exchange of the CH$_3$CO$_2$ ligands for CD$_3$CO$_2$.

Reaction of [5][PF$_6$] with Propionic Acid. To a 25-mL Erlenmeyer flask were added [5][PF$_6$] (1.00 g; 1.1 mmol) and 9 mL of propionic acid. The resulting suspension was heated to boiling and allowed to cool to ambient temperature. The mixture was filtered, and the solid residue that was collected contained blue crystals (presumably cobaltous propionate) mixed with the dark brown crystals to the product. The residue was washed with 5 mL of cold water, which removed the blue material. The yield was 453 mg of [(py)$_3$Co$_3$O(CH$_3$CH$_2$CO$_2$)$_6$][PF$_6$]. Anal. Calcd for C$_{33}$H$_{45}$Co$_3$F$_6$N$_3$O$_{13}$P: C, 39.09; H, 4.44; N, 4.15; Co, 17.47. Found: C, 38.67; H, 4.41; N, 3.87; Co, 17.7. ^{1}H NMR (400 MHz; CD$_2$Cl$_2$): δ 8.95 (d, 6 H), 8.02 (t, 3 H), 7.65 (t, 6 H), 2.35 (qt, 12 H), 0.95 (t, 18 H). The FAB mass spectrum displayed ions at m/e 868 for the [(py)$_3$Co$_3$O(CH$_3$CH$_2$CO$_2$)$_6$]$^+$ ion and m/e 789, 710, etc. corresponding to the successive loss of two pyridine ligands, two propionates, a pyridine, and a propionate.

X-ray Crystallographic Studies of [(py)$_4$Co$_2$(OAc)$_3$(OH)$_2$][PF$_6$]·2CH$_2$Cl$_2$, [3][PF$_6$], and [(py)$_5$Co$_3$O(OAc)$_3$(OH)$_2$][PF$_6$]$_2$·CH$_2$Cl$_2$·H$_2$O, [4][PF$_6$]$_2$.[8] Large, well-shaped violet single crystals of [3][PF$_6$] and black single crystals of [4][PF$_6$]$_2$ obtained as described above were suitable for X-ray diffraction studies. At 20 ± 1 °C, crystals of both compounds are monoclinic, with $a = 12.478$ (2) Å, $b = 14.223$ (3) Å, $c = 23.278$ (4) Å, $\beta = 103.92$ (1)°, $V = 4010$ (1) Å^3, and $Z = 4$ [μ_a(Mo Kα)^{13a} = 1.21

mm^{-1}; $d_{calcd} = 1.590$ g cm^{-3}] for **3** and $a = 16.500$ (3) Å, $b = 17.128$ (4) Å, $c = 17.357$ (4) Å, $\beta = 105.64$ (2)°, $V = 4724$ (2) Å^3, and $Z = 4$ [μ_a(Mo Kα)^{13a} = 1.32 mm^{-1}; $d_{calcd} = 1.68$ g cm^{-3}] for **4**[PF$_6$]$_2$. The space group for both compounds was uniquely determined by the systematically absent reflections as centrosymmetric $P2_1/c$-C_{2h}, No. 14,[14] for [3][PF$_6$] and centrosymmetric $P2_1/n$ (an alternate setting of $P2_1/c$) for [4][PF$_6$]$_2$.

Intensity measurements for both compounds were made on a computer-controlled Nicolet autodiffractometer using full (1.00° ([3][PF$_6$]) or 0.90° ([4][PF$_6$]$_2$) wide) ω scans and graphite-monochromated Mo Kα radiation for rectangular parallelepiped-shaped specimens having dimensions of 0.45 × 0.50 × 0.73 mm ([3][PF$_6$]) and 0.30 × 0.32 × 0.50 mm ([4][PF$_6$]$_2$). The crystal of [3][PF$_6$] was glued with epoxy to the inside of a thin-walled glass capillary, and the crystal of [4][PF$_6$]$_2$ was glued to the end of a thin glass fiber having a tip diameter of 0.18 mm. Both crystals were mounted on a goniometer with their longest edge nearly parallel with the φ axis of the diffractometer. Totals of 9235 ([3][PF$_6$]) and 8646 ([4][PF$_6$]$_2$) independent reflections having 3° < $2\theta_{Mo Kα}$ < 55° ([3][PF$_6$]) or 3° < $2\theta_{Mo Kα}$ < 50.7° ([4][PF$_6$]$_2$) (the equivalent of 1.0 ([3][PF$_6$]) or 0.80 ([4][PF$_6$]$_2$) Cu Kα limiting spheres) were measured for both compounds with scanning rates of 6 or 4°/min for [3][PF$_6$] and 6 or 2°/min for [4][PF$_6$]$_2$. The data collection and reduction procedures that were used are described elsewhere.[15]

The two crystallographically independent Co atoms and one P atom in the asymmetric unit of [3][PF$_6$] and the three Co atoms of [4][PF$_6$]$_2$ were located using (SHELXTL) "direct-methods" techniques. Counter-weighted[18] full-matrix least-squares refinement of the structural parameters for the two isotropic Co atoms and one P atom in [3][PF$_6$] gave R_1 (unweighted, based on F)^{16} = 0.486 for 3333 independent reflections having $I > 3\sigma(I)$ and $2\theta_{Mo Kα}$ < 43°. Similar refinement of the three isotropic Co atoms in [4][PF$_6$]$_2$ gave R_1 = 0.420 for 5269 independent reflections having $I > 3\sigma(I)$ and $2\theta_{Mo Kα}$ < 50.7°.

Difference Fourier syntheses for both structures based on the models containing two isotropically refined Co atoms and one P atom for [3]-[PF$_2$] and three isotropically refined Co atoms for [4][PF$_6$]$_2$ revealed the remaining 50 ([3][PF$_6$]) and 64 ([4][PF$_6$]$_2$) non-hydrogen atoms of the respective asymmetric units. Inclusion of these atoms into the model with isotropic thermal parameters gave R_1 = 0.106 for 3333 reflections of [3][PF$_6$] and R_1 = 0.093 for 5269 reflections of [4][PF$_6$]$_2$. Subsequent counter-weighted cascade block-diagonal least-squares refinement cycles, which utilized anisotropic thermal parameters for all non-hydrogen atoms, gave R_1 = 0.063 for 3333 reflections of [3][PF$_6$] and R_1 = 0.060 for 5269 reflections of [4][PF$_6$]$_2$.

Hydrogen atoms for both compounds were located from difference Fourier syntheses based on these fully refined anisotropic models. Hydrogen atoms of the bridging hydroxy groups of both compounds were refined as independent atoms while the methyl groups were refined as rigid rotors with idealized sp^3-hybridized geometry and a C–H bond length of 0.96 Å. The initial orientation of each methyl group was determined from difference Fourier positions for the hydrogens; the final orientation of each methyl group was determined by three rotational parameters. Idealized positions for the pyridine hydrogens of the cations and the CH$_2$Cl$_2$ hydrogens of the solvent molecules in [3][PF$_6$] and [4][PF$_6$]$_2$ were calculated by assuming sp^2 or sp^3 hybridization of the carbon and a C–H bond length of 0.96 Å and fixed in subsequent refinement cycles. All hydrogen atoms except those of the bridging hydroxy groups were included in all subsequent structure factor calculations with isotropic thermal parameters that were fixed at 1.2 times the equivalent isotropic thermal parameter of the carbon to which they are

(13) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol, IV: (a) pp 55–66; (b) pp 99–101; (c) pp 149–150.

(14) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1969; Vol. I, p 99.

(15) Burch, R. R.; Muetterties, E. L.; Day, V. W. *Organometallics* **1982**, *I*, 188.

(16) The R values are defined as $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ where $w (=1/\sigma_F{}^2)$ is the weight given each reflection. The function minimized is $\sum w(|F_o| - K|F_c|)^2$, where K is the scale factor.

covalently bonded. The isotropic thermal parameters for the hydrogens of the bridging hydroxy groups refined to final values of 5 (1) and 8 (1) Å² for [3][PF₆] and 2 (1) and 3 (1) Å² for [4][PF₆]₂. All subsequent structure factor calculations for both compounds employed a least-squares refinable extinction correction.[17]

The final cycles of counter-weighted[18] cascade block-diagonal least-squares refinement, which employed anisotropic thermal parameters for all non-hydrogen atoms and isotropic thermal parameters for all hydrogen atoms, gave R_1 = 0.047 and R_2 (weighted, based on F)[16] = 0.046 for 5205 independent reflections of [3][PF₆] having $2\theta_{Mo\,K\alpha}$ < 55° and I > $3\sigma(I)$. Similar refinement cycles for [4][PF₆]₂ gave R_1 = 0.050 and R_2 = 0.049 for 5269 independent reflections having $2\theta_{Mo\,K\alpha}$ < 50.7° and I > $3\sigma(I)$.

All structure factor calculations for both compounds employed recent tabulations of atomic form factors[13b] and anomalous dispersion corrections[13c] to the scattering factors of the Co, Cl, P, and F atoms. All calculations were performed on a Data General Eclipse S-200 or S-230 computer equipped with 256K of 16-bit words, a floating point processor

for 32- and 64-bit arithmetic, and versions of the Nicolet EXTL and SHELXTL interactive crystallographic software packages as modified at the Crystalytics Co.

(17) Larson, A. C. *Acta Crystallogr.* **1967**, *23*, 664.
(18) For counter weights: $\sigma_F = \{[\sigma(F_o)]^2 + (p|F_o|)^2\}^{1/2}$ where the "ignorance factor", p, has the value of 0.01 in this case.

Tri- and Tetranuclear Palladium–Cobalt Clusters Containing Bridging Ph₂PCH₂PPh₂ (dppm) Ligands. Crystal Structures of [Pd₂Co₂(μ₃-CO)₂(CO)₅(μ-dppm)₂] and [Pd₂Co(μ₃-CO)₂(CO)₂(μ-dppm)₂][PF₆]

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The heterotetranuclear cluster [Pd₂Co₂(CO)₇(dppm)₂] (**1**) was synthesized in high yield by the reaction of [Co(CO)₄]⁻ with [Pd₂Cl₂(dppm)₂] (dppm = μ-Ph₂PCH₂PPh₂), whereas the A-frame complexes [Pd₂Cl₂(μ-Y)(dppm)₂] (Y = CO, CH₂) are much less reactive. The molecular structure of **1**·2.5THF has been determined by X-ray diffraction. Crystal data: triclinic, space group $P\bar{1}$ with Z = 2, a = 18.417 (8) Å, b = 14.798 (6) Å, c = 13.855 (6) Å, α = 113.61 (2)°, β = 107.50 (2)°, γ = 82.20 (2)°, V = 3299 Å³, R = 0.055, R_w = 0.076. This cluster contains a metalloligated triangular core of which two edges are bridged by the dppm ligands in such a way that the four P atoms and the four metal atoms are almost coplanar. The lability of the P→Pd bond of the precursor complex accounts for the easy formal insertion of the Co(CO)₃ fragment into this bond. A metal-exchange reaction can be thermally induced that transforms **1** into the triangular cluster [PdCo₂(CO)₅(dppm)₂]. The reaction of **1** with anionic nucleophiles X⁻ was found to regioselectively break the exocyclic Pd–Co bond, and it afforded the clusters [Pd₂CoX-(CO)₃(dppm)₂] (X = Cl, Br, I, OH, SCN). The reversibility of this reaction was investigated, and the reaction leading to the halogeno clusters was best carried out in acetone, proceeding faster depending upon the nature of X⁻ (I⁻ ≈ Br⁻ >> Cl⁻) and of the corresponding cation (PPN⁺ >> K⁺, Na⁺). Re-formation of the exocyclic Pd–Co bond was observed in Et₂O. The cationic cluster [Pd₂Co(CO)₄(dppm)₂]⁺ was prepared by carbonylation of the halide-substituted Pd₂Co clusters in the presence of a halide abstractor. Its unique Pd-bound terminal CO ligand is very labile and can be reversibly and selectively replaced by a solvent molecule (acetone, THF, MeCN) depending upon CO partial pressure. The molecular structure of [Pd₂Co(CO)₄(dppm)₂]-[PF₆]·C₃H₆O (**7**·acetone) has been determined by X-ray diffraction. Crystal data: monoclinic, space group Cc with Z = 4, a = 22.87 (2) Å, b = 14.198 (4) Å, c = 22.27 (2) Å, β = 122.35 (5)°, V = 6109 Å³, R = 0.053, R_w = 0.069. The structure of the cation may be considered as derived from that of **1** by the replacement of the terminally bound Co(CO)₄ unit by a carbonyl group. Spectroscopic IR and ¹H and ³¹P{¹H} NMR data are discussed in relation with the structure and reactivity of these new clusters. The synthesis and chemistry of **1** are characterized by reactions formally taking place within the Pd₂P₄ plane. The bonding description of the clusters with a Pd₂Co(dppm)₂ core emphasizes their belonging to a new class of clusters where an anionic 18-electron metal carbonyl fragment is part of a closo structure.

Introduction

Bis(diphenylphosphino)methane (dppm), first synthesized by Issleib and Müller in 1959,[1] is presently playing a key role as a small-bite bidentate ligand in di- and polynuclear chemistry.[2,3] This ligand is remarkably versatile in its properties, allowing the stabilization of, e.g., dinuclear metal–metal-bonded complexes (A), A-frame complexes (B), double A-frame (C) complexes, or

face-to-face eight-membered dimetallocycles M₂(μ-dppm)₂ (D), just to name examples where trans P–M–P arrangements are found.

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