

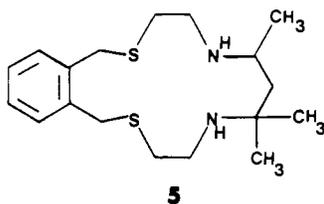
second being slower than the first. Although other interpretations are possible, in view of the known stepwise dissociation of other macrocyclic systems,¹⁹ the present data were treated according to



By means of a computer fit, values of k_1 and k_2 which best reproduced the observed absorbance values were obtained (Table II). The value of k_1 is about 1 order of magnitude greater than k_2 , and both constants are considerably smaller than the first-order dissociation rate constant ($3.5 \times 10^{-3} \text{ s}^{-1}$) determined previously, under identical conditions, for the nickel complex of the analogous O_2N_2 macrocycle (**1**, $n = 3$ and $m = 2$).⁸ Both steps show no significant acid dependence, and both are accelerated in the presence of acetate²⁰—results which once again parallel observations made for the previously studied O_2N_2 system. The small difference between the values of k_1 (and also of k_2) which were obtained in H_2O and D_2O are also in accord with the acid independence of the dissociation.

The similarity of the ΔH^\ddagger values obtained for the two steps (Table II) suggests that they reflect successive removal of similar donor atoms from the nickel. The observed acid independence of both steps together with the markedly slower dissociation rates relative to that of the analogous O_2N_2 -donor complex further suggest that it is the dissociation of the sulfur donor atoms which are observed in the present study.

A recent study⁶ of the kinetics of dissociation of the related nickel complex of **5** yielded a single first-order dissociation



constant of $2.8 \times 10^{-5} \text{ s}^{-1}$ (25 °C; $I = 0.5$). Once again the dissociation was found to be acid independent, and thus this appears to be a characteristic of the dissociation of nickel complexes of the X_2N_2 -donor ($\text{X} = \text{O}, \text{S}$) macrocycles studied so far.^{6,8}

Acknowledgment. We acknowledge the Australian Institute for Nuclear Science and Engineering for a travel grant and the Australian Research Grants Committee for support. We thank Dr. J. T. Baker of the Roche Research Institute of Marine Pharmacology, Sydney, Australia, for assistance.

Registry No. 2·2HCl, 76124-43-1; 3·2HCl, 76124-44-2; 4·2HCl, 76124-45-3; $\text{Ni}_2(14\text{-MAC})\text{Cl}_4$, 76299-34-8; $\text{Ni}(15\text{-MAC})\text{Cl}_2$, 76137-02-5; $\text{Ni}(16\text{-MAC})\text{Cl}_2$, 76137-03-6; 1,4-bis(2-benzyl alcohol)-1,4-dithiabutane, 76124-46-4; 1,5-bis(2-benzyl alcohol)-1,5-dithiapentane, 76124-47-5; 1,4-bis(2-formylphenyl)-1,4-dithiabutane, 25676-67-9; 1,5-bis(2-formylphenyl)-1,5-dithiabutane, 76124-48-6; 1,4-bis(2-carboxyphenyl)-1,4-dithiabutane, 52961-83-8; 1,5-bis(2-carboxyphenyl)-1,5-dithiapentane, 76124-49-7; 1,2-diaminoethane, 107-15-3; 1,3-diaminopropane, 109-76-2.

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(20) Previously, we have shown⁸ that the presence of acetate ion leads to an increase in the first-order dissociation rate of the nickel complex of the O_2N_2 macrocyclic ligand (**1**, $n = 3$ and $m = 2$). During the present study we have carried out a parallel investigation in which the dissociation of the analogous complex of ligand **3** in acetic acid (1 M)/sodium acetate (1 M) buffer (pH 4.5—the same conditions as used for the previous study) was followed. As before, enhanced dissociation was observed; under these conditions the respective values for k_1 and k_2 are $(2.7 \pm 0.2) \times 10^{-3} \text{ s}^{-1}$ and $(5.6 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$. However, as discussed in ref 8, the mechanism of the rate enhancement by acetate remains uncertain.

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Crystal and Molecular Structure of $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P}(\text{OCH}_3)_3]_3$. An Example of Highly Unsymmetrical Bonding of an η^3 -Benzyl Ligand

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$(\eta^3\text{-L})\text{Co}(\text{phosphite})_3$ complexes (L = allyl, cyclooctenyl, benzyl) have been shown to be catalyst precursors for the homogeneous hydrogenation of aromatic hydrocarbons.² Although the catalytic chemistry and spectroscopic properties of this series of compounds have been studied extensively, their structural chemistry has not been described. We now wish to report the crystal and molecular structure of $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P}(\text{OCH}_3)_3]_3$, a compound of particular interest because it possesses a simple benzyl ligand in the relatively unusual η^3 bonding mode.³

Experimental Section

A. Collection of X-ray Diffraction Data. Red-brown needles of $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ ^{3e} were grown from a saturated methanol solution at -40°C . A crystal of dimensions $0.40 \times 0.23 \times 0.10 \text{ mm}$ was mounted in a thin-walled, 0.3-mm glass capillary under argon. Preliminary precession photographs indicated $2/m$ Laue symmetry with systematic absences $h0l$, $l = 2n + 1$, and $0k0$, $k = 2n + 1$, consistent with the monoclinic space group $P2_1/c$.

The crystal was mounted on a Nonius CAD-4 four-circle, κ -geometry diffractometer automated by a PDP8-E minicomputer and Enraf-Nonius structure determination package.⁴ A preliminary orientation matrix was determined by searching reciprocal space in the region near $2\theta = 12^\circ$ and indexing the reflections found.

Accurate cell dimensions and orientation matrix were determined by centering 24 reflections (6 sets of 4 symmetry-related reflections) with 2θ values between 23.64 and 24.98° . Table I gives the derived crystal parameters and details of the data collection procedure.

All data reduction and structure refinement was done on the University of California at Berkeley Chemistry Department X-Ray Facility's PDP 11/60 computer using local modifications of the Enraf-Nonius structure determination package.⁴ The 3534 reflections collected were reduced to structure factor amplitudes and their esds by corrections for Lorentz and polarization effects, scan time, and background. Inspection of the standard reflections showed a maximum decay of 7.2% in F_o . All intensities were scaled accordingly. Observations of the intensities of several reflections [(051), (061), (020)] near $\chi = 90^\circ$ at 10° increments of rotation around the diffraction vectors showed a maximum variation of $\sim 8\%$. Absorption corrections were performed with use of the calculated absorption coefficient ($\mu = 9.9 \text{ cm}^{-1}$), the Miller indices of the faces bounding the crystal [(021), (0, -2, -1), (102), (-1, 0, -2), (1, 0, -2), (-1, 0, 2)], and the dimensions of these faces. Reflections equivalent by Laue symmetry were averaged and those corresponding to systematic absences were deleted to yield

- (1) To whom correspondence should be addressed.
- (2) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 4063. Rakowski, M. C.; Hirsekorn, F. J.; Stuhl, L. S. Muetterties, E. L. *Inorg. Chem.* **1976**, *15*, 2379. Bleeker, J. R.; Muetterties, E. L. *Acc. Chem. Res.* **1979**, *12*, 324.
- (3) Only a few η^3 -benzyl-M complexes are known, and in most of these the benzyl moiety is part of a larger aromatic system. Syntheses of η^3 -benzyl-M complexes are described: (a) Wilke, G.; Schott, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 583. (b) King, R. B.; Fronzaglia, A. J. *Am. Chem. Soc.* **1966**, *88*, 709. (c) O'Connor, C. J. *Inorg. Nucl. Chem.* **1970**, *32*, 2299. (d) Stevens, R. R.; Shier, G. D. *J. Organomet. Chem.* **1970**, *21*, 495. (e) Muetterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* **1974**, *96*, 7920. (f) Roberts, J. S.; Klabunde, K. J. *J. Organomet. Chem.* **1975**, *85*, C13. Roberts, J. S.; Klabunde, K. J. *J. Am. Chem. Soc.* **1977**, *99*, 2509. (g) Sonada, A.; Mann, B. E.; Maitlis, P. M. *J. Chem. Soc., Chem. Commun.* **1975**, 108. Mann, B. E.; Keasey, A.; Sonada, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1979**, 338. (h) Behrens, U.; Weiss, E. *J. Organomet. Chem.* **1975**, *96*, 399. (i) Behrens, U.; Weiss, E. *Ibid.* **1975**, *96*, 435.
- (4) Frenz, B. "Structure Determination Package User's Guide", 3rd ed.; Enraf-Nonius: Delft, April 1980.

Table I. Data for X-ray Diffraction Study of $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P}(\text{OCH}_3)_3]_3$

A. Crystal Data			
space group	$P2_1/c$ (No. 14)	$V, \text{\AA}^3$	2388.4 (9)
$a, \text{\AA}$	10.782 (1)	Z	4
$b, \text{\AA}$	8.687 (1)	$\rho(\text{calcd}), \text{g/cm}^3$	1.452
$c, \text{\AA}$	25.521 (3)	$T, ^\circ\text{C}$	22
β, deg	92.40 (1)		

B. Intensity Data	
radiation	Mo $K\alpha$ ($\lambda = 0.71073 \text{\AA}$) ^a
reflectns measd	$+h, +k, \pm l$
2θ range, deg	3–45
scan type	θ - 2θ
scan time	variable, with max of 75 s
scan:bkgd time	2:1
absorption coeff (μ, cm^{-1})	9.9
transmission factors	90.78 (max), 75.42 (min)
stds	(053), (612), (2,0,-14) ^b

^a Graphite monochromatized. ^b These three reflections were checked every 7200 s for loss of intensity and every 50 reflections for orientation. (A new orientation matrix was calculated if the setting angles changed by more than 0.1° in any axis.)

3104 unique reflections of which 2393 had intensities greater than 3 times their esd's and were used in the least-squares refinement.

B. Solution and Refinement of Structure.⁵ The cobalt atom was located from a three-dimensional Patterson map. One cycle of least-squares refinement based on the cobalt atom position followed by the synthesis of a three-dimensional Fourier map revealed the locations of the three phosphorus atoms and six of the oxygen atoms. Two more cycles of least-squares refinement and a Fourier synthesis revealed the positions of the remaining nonhydrogen atoms. With the positions of all 29 nonhydrogen atoms included, several cycles of isotropic least-squares refinement led to the agreement indices $R = 0.081$ and $R_w = 0.11$ (GOF = 5.3). Anisotropic thermal parameters were then included, and several least-squares cycles led to agreement indices $R = 0.049$ and $R_w = 0.070$ (GOF = 3.1). The synthesis of a difference Fourier map at this point revealed the locations of six of the seven benzyl hydrogen atoms. All seven benzyl hydrogen atoms were added at idealized positions with a C–H distance of 0.95 Å. Their isotropic thermal parameters were set at $B = 5.0 \text{\AA}^2$. Anisotropic least-squares refinement on the nonhydrogen atoms led to convergence with $R = 0.046$, $R_w = 0.070$, and GOF = 3.0. A difference Fourier synthesis led to the location of about half of the methyl hydrogen atoms. These hydrogen atoms were staggered with respect to the P–O bond, so all 27 methyl hydrogen atoms were added at idealized (staggered) positions with a C–H distance of 0.95 Å. Their isotropic thermal parameters were set at $B = 12.0 \text{\AA}^2$. Continued anisotropic refinement on the nonhydrogen atoms led to final convergence with $R = 0.032$, $R_w = 0.041$, R for all reflections including unobserved reflections equal to 0.054, and GOF = 1.7 (262 variables, 2393 observations). A final difference Fourier map yielded no peaks greater than $0.22 \text{ e}/\text{\AA}^3$.

Results and Discussion

A perspective view of $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ is presented in the ORTEP drawing in Figure 1. Atomic coordinates and anisotropic thermal parameters for the nonhydrogen atoms are listed in Table II; important bond distances and bond angles are listed in Table III.

The structure of $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ approximates a trigonal bipyramid, as documented by several features of the structure. The $\text{C}_1\text{-Co-P}_2$ and $\text{C}_1\text{-Co-P}_3$ angles are close

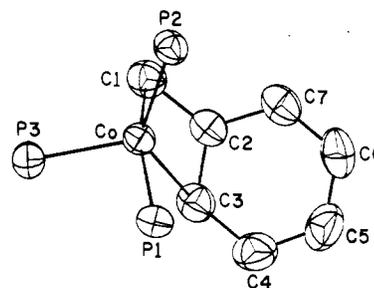


Figure 1. ORTEP drawing of $(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Co}[\text{P}(\text{OCH}_3)_3]_3$ viewed approximately down the pseudo-3-fold axis. The η^3 -benzyl group spans the back axial site (C_1) and lower right equatorial site (C_3). Methoxy groups of the phosphite ligands and hydrogen atoms of the benzyl ligand have been removed for clarity.

to 90° as are the $\text{P}_1\text{-Co-P}_2$ and $\text{P}_1\text{-Co-P}_3$ angles, suggesting that C_1 and P_1 occupy axial positions while P_2 , P_3 , and C_3 occupy equatorial sites. The equatorial plane is defined by Co , C_3 , P_2 , and P_3 , with the largest deviation from that plane being the position of the cobalt atom, which is displaced 0.215\AA toward P_1 . The dihedral angles between the equatorial plane defined by $\text{P}_2\text{-P}_3\text{-C}_3$ and the planes $\text{P}_1\text{-Co-P}_2$, $\text{P}_1\text{-Co-P}_3$, and $\text{P}_1\text{-Co-C}_3$ are all near the ideal 90° (89.2 , 90.1 , and 89.1° , respectively), further supporting the trigonal-bipyramidal characterization of the coordination sphere.

The steric demand of the benzyl ligand manifests itself in distortions from the trigonal-bipyramidal geometry. The small bite angle of the benzyl ligand results in a $\text{C}_1\text{-Co-C}_3$ angle substantially less than the ideal 90° ($\text{C}_1\text{-Co-C}_3 = 65.77^\circ$) and a $\text{C}_1\text{-Co-P}_1$ angle less than 180° ($\text{C}_1\text{-Co-P}_1 = 161.85^\circ$). Although the angle between the two equatorial phosphorus atoms is close to the ideal 120° ($\text{P}_2\text{-Co-P}_3 = 121.78^\circ$), the remaining interligand angles in the equatorial plane are distorted—enlarged on one side of the molecule ($\text{C}_3\text{-Co-P}_2 = 133.72^\circ$) and contracted on the other ($\text{C}_3\text{-Co-P}_3 = 99.13^\circ$). This distortion appears to be due to steric interaction between the benzyl ring and methoxy groups attached to P_2 that forces the $\text{C}_3\text{-Co-P}_2$ angle open (Figure 1).

The Co-C_1 distance is 0.372\AA shorter than the Co-C_3 distance in this structure (2.036 vs. 2.408\AA). The shortness of the metal- α -carbon distance with respect to the metal-ortho carbon distances in a π -benzyl structure is expected because of the greater negative charge that resides on the α -carbon of the benzyl anion,⁷ but the 0.372-\AA difference observed in this structure is significantly larger than has previously been observed. For example, the difference is 0.21\AA in $(\eta^3\text{-CH}_2\text{C}_6\text{H}_4\text{CH}_3)\text{Mo}(\text{C}_6\text{H}_5)(\text{CO})_2$ in which $\text{Mo-}\alpha\text{-C} = 2.269$ (7) Å and $\text{Mo-ortho C} = 2.480$ (6) Å,⁸ while the differences are only 0.095 and 0.060\AA in $\eta^3\text{-C}(\text{C}_6\text{H}_5)_3\text{M}(\text{acetylacetonate})$ ($\text{M} = \text{Pd, Pt, respectively}$)⁹ and 0.122 and 0.105\AA in $(\text{diphenylfulvalene})\text{M}_2(\text{pentacarbonyl})$ ($\text{M} = \text{Fe, Ru, respectively}$).^{3b,i}

(5) The atomic form factors for neutral atoms were taken from ref 6a. All except those for hydrogen were corrected for the real and imaginary components of anomalous dispersion for Mo radiation.^{6b} The quantity minimized by least squares was $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/(\sigma_c^2(F_o^2) + (pF_o^2)^2)$ and $\sigma_c(F_o)$ is based solely on counting statistics. The parameter p , introduced to prevent overweighing of strong reflections, was set to 0.03. Agreement indices are defined as $R = \sum |F_o| - |F_c| / \sum |F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$. The "goodness-of-fit" (GOF) is defined as $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$. Here N_o is the number of observations and N_v is the number of variables.

(6) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV: (a) Table 2.2B; (b) Table 2.3.1.

(7) We have performed an extended Hückel molecular orbital calculation on the benzyl monoanion in an idealized geometry and in the geometry observed in this structure. The results show that the majority of the formal negative charge (0.876 e in the idealized geometry and 0.911 e in the observed structure) resides on the α -carbon. The formal negative charge on the bound ortho carbon (C_3) in the idealized and observed structures is 0.252 and 0.273 e , respectively. Thus, the asymmetric binding of the benzyl ligand to the cobalt atom is a consequence of the much greater negative charge on the α -carbon, and the distortion of the benzyl ligand occurs in such a way that the formal negative charge on the α -carbon and the ortho carbon bound to the cobalt atom increases. The same argument applies if the benzyl ligand is considered to be formally a cation or a free radical. In these cases, the LUMO has largest density on the α -carbon; hence, maximum metal-ligand orbital overlap is expected at the α -carbon.

(8) Cotton, F. A.; LaPrade, M. D. *J. Am. Chem. Soc.* **1968**, *90*, 5418.
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Table II. Final Positional and Anisotropic Thermal Parameters^a (with Esd's)^b for the Nonhydrogen Atoms of (η^3 -CH₂C₆H₅)Co[P(OCH₃)₃]₃

atom	x	y	z	B(1,1)	B(2,2)	B(3,3)	B(1,2)	B(1,3)	B(2,3)
Co	0.24684 (4)	0.22518 (5)	0.11403 (2)	3.00 (2)	2.60 (2)	2.72 (2)	-0.12 (2)	0.26 (2)	0.08 (2)
P ₁	0.30474 (9)	0.3617 (1)	0.17957 (4)	3.83 (4)	3.00 (4)	2.83 (4)	0.01 (4)	0.20 (3)	0.07 (4)
P ₂	0.26677 (9)	0.3966 (1)	0.05538 (4)	3.42 (4)	3.10 (4)	3.17 (4)	0.19 (4)	0.46 (3)	0.52 (4)
P ₃	0.07092 (9)	0.1579 (1)	0.13927 (4)	2.95 (4)	4.14 (5)	3.79 (4)	-0.03 (4)	0.34 (3)	0.33 (4)
O ₁₁	0.4496 (2)	0.3774 (3)	0.19651 (9)	4.2 (1)	5.8 (2)	3.6 (1)	-0.8 (1)	-0.2 (1)	-0.6 (1)
O ₁₂	0.2566 (3)	0.5352 (3)	0.17717 (10)	6.5 (1)	2.9 (1)	3.9 (1)	0.3 (1)	0.1 (1)	-0.2 (1)
O ₁₃	0.2602 (2)	0.3231 (3)	0.23768 (9)	5.8 (1)	3.7 (1)	2.9 (1)	0.4 (1)	0.7 (1)	0.3 (1)
O ₃₁	0.0072 (2)	0.2192 (4)	0.19166 (11)	4.4 (1)	6.6 (2)	4.8 (1)	0.8 (1)	1.2 (1)	-0.0 (1)
O ₃₂	-0.0511 (2)	0.1824 (4)	0.10152 (11)	3.3 (1)	9.1 (2)	5.2 (1)	-0.2 (1)	-0.3 (1)	0.7 (2)
O ₃₃	0.0616 (2)	-0.0231 (3)	0.15307 (11)	3.9 (1)	4.2 (1)	7.4 (2)	-1.0 (1)	1.5 (1)	1.2 (1)
O ₂₁	0.1519 (2)	0.5058 (3)	0.03722 (10)	3.9 (1)	6.2 (2)	5.0 (1)	1.5 (1)	0.5 (1)	2.2 (1)
O ₂₂	0.2932 (3)	0.3343 (4)	-0.00212 (10)	10.6 (2)	5.1 (1)	3.3 (1)	1.2 (2)	2.2 (1)	0.8 (1)
O ₂₃	0.3742 (2)	0.5206 (3)	0.06539 (11)	4.4 (1)	3.9 (1)	7.2 (2)	-1.1 (1)	-0.5 (1)	2.4 (1)
C ₁₁	0.5422 (4)	0.4038 (6)	0.1594 (2)	4.1 (2)	6.8 (3)	4.7 (2)	-1.5 (2)	0.2 (2)	-1.0 (2)
C ₁₂	0.2814 (5)	0.6428 (5)	0.2193 (2)	11.0 (3)	3.4 (2)	5.4 (2)	0.1 (2)	0.5 (2)	-1.1 (2)
C ₁₃	0.2846 (4)	0.1783 (5)	0.2609 (2)	7.6 (3)	4.8 (2)	3.9 (2)	1.0 (2)	0.8 (2)	1.3 (2)
C ₃₁	-0.0442 (5)	0.3669 (6)	0.1948 (2)	7.6 (3)	6.7 (3)	7.5 (3)	1.5 (2)	2.6 (2)	-0.3 (3)
C ₃₂	-0.0524 (4)	0.1788 (7)	0.0465 (2)	5.1 (2)	9.3 (3)	4.6 (2)	-0.2 (2)	-1.0 (2)	0.0 (2)
C ₃₃	-0.0531 (4)	-0.0997 (6)	0.1621 (2)	5.9 (2)	6.6 (3)	9.3 (3)	-2.4 (2)	2.9 (2)	0.7 (3)
C ₂₁	0.0765 (4)	0.5808 (6)	0.0731 (2)	5.7 (2)	6.7 (3)	6.1 (2)	2.9 (2)	1.0 (2)	1.4 (2)
C ₂₂	0.2816 (5)	0.4100 (8)	-0.0502 (2)	7.6 (3)	13.5 (4)	4.0 (2)	2.0 (3)	0.6 (2)	1.5 (3)
C ₂₃	0.3862 (5)	0.6668 (6)	0.0437 (2)	5.9 (2)	4.0 (2)	12.0 (4)	-0.4 (2)	0.3 (3)	2.4 (3)
C ₁	0.2368 (4)	0.0527 (5)	0.0600 (1)	4.4 (2)	3.9 (2)	3.4 (2)	0.4 (2)	0.4 (1)	-0.4 (2)
C ₂	0.3571 (3)	0.0434 (4)	0.0861 (1)	4.0 (2)	2.5 (2)	3.3 (2)	0.2 (1)	0.7 (1)	-0.5 (1)
C ₃	0.3634 (4)	-0.0015 (5)	0.1390 (1)	4.2 (2)	3.7 (2)	4.1 (2)	0.8 (2)	0.7 (1)	0.2 (2)
C ₄	0.4799 (4)	-0.0134 (5)	0.1659 (2)	5.5 (2)	5.5 (2)	4.2 (2)	1.5 (2)	-0.1 (2)	0.4 (2)
C ₅	0.5857 (4)	0.0149 (6)	0.1410 (2)	3.7 (2)	6.7 (3)	6.3 (2)	1.5 (2)	-0.3 (2)	-0.7 (2)
C ₆	0.5808 (4)	0.0645 (5)	0.0887 (2)	3.7 (2)	5.8 (2)	6.3 (2)	0.5 (2)	1.8 (2)	-0.9 (2)
C ₇	0.4692 (4)	0.0812 (5)	0.0627 (1)	4.9 (2)	3.5 (2)	4.0 (2)	0.6 (2)	1.2 (2)	-0.4 (2)

^a The form of the anisotropic thermal ellipsoid is $\exp[-(B(1,1)h^2a^{*2} + B(2,2)k^2b^{*2} + B(3,3)l^2c^{*2} + 2B(1,2)hka^{*}b^{*} + 2B(1,3)hla^{*}c^{*} + 2B(2,3)klb^{*}c^{*})/4]$. ^b Numbers in parentheses are the estimated standard deviations and refer to the last significant digit of the preceding number.

Table III. Interatomic Distances (Å) and Angles (Deg) (with Esd's) for (η^3 -CH₂C₆H₅)Co[P(OCH₃)₃]₃

Distances		
Co-P ₁	2.123 (1)	C ₅ -C ₆ 1.401 (5)
Co-P ₂	2.129 (1)	C ₆ -C ₇ 1.357 (4)
Co-P ₃	2.111 (1)	C ₁ -C ₇ 1.409 (4)
Co-C ₁	2.036 (3)	P ₁ -O ₁₁ 1.609 (2)
Co-C ₂	2.117 (3)	P ₁ -O ₁₂ 1.595 (2)
Co-C ₃	2.408 (3)	P ₁ -O ₁₃ 1.613 (2)
C ₁ -C ₂	1.435 (4)	O ₁₁ -C ₁₁ 1.423 (4)
C ₂ -C ₃	1.404 (4)	O ₁₂ -C ₁₂ 1.442 (4)
C ₃ -C ₄	1.409 (4)	O ₁₃ -C ₁₃ 1.410 (4)
C ₄ -C ₅	1.352 (5)	
Angles		
C ₁ -Co-C ₂	40.36 (11)	C ₁ -C ₂ -C ₃ 117.97 (27)
C ₁ -Co-C ₃	65.77 (11)	C ₁ -C ₂ -C ₇ 124.34 (28)
C ₁ -Co-P ₁	161.85 (9)	C ₂ -C ₃ -C ₄ 119.68 (28)
C ₁ -Co-P ₂	92.44 (9)	C ₃ -C ₄ -C ₅ 120.71 (31)
C ₁ -Co-P ₃	88.87 (9)	C ₄ -C ₅ -C ₆ 120.27 (31)
C ₂ -Co-C ₃	35.41 (10)	C ₅ -C ₆ -C ₇ 119.75 (31)
C ₂ -Co-P ₁	122.07 (8)	C ₆ -C ₇ -C ₂ 121.76 (30)
C ₂ -Co-P ₂	102.14 (8)	C ₇ -C ₂ -C ₃ 117.65 (27)
C ₂ -Co-P ₃	114.86 (8)	Co-P ₁ -O ₁₁ 120.62 (9)
C ₃ -Co-P ₁	96.63 (8)	Co-P ₁ -O ₁₂ 114.40 (8)
C ₃ -Co-P ₂	133.72 (8)	Co-P ₁ -O ₁₃ 121.28 (9)
C ₃ -Co-P ₃	99.13 (8)	P ₁ -O ₁₁ -C ₁₁ 122.35 (18)
P ₁ -Co-P ₂	97.37 (3)	P ₁ -O ₁₂ -C ₁₂ 122.29 (21)
P ₁ -Co-P ₃	98.77 (3)	P ₁ -O ₁₃ -C ₁₃ 120.96 (19)
P ₂ -Co-P ₃	121.78 (3)	

There is a C-C bond length alternation in the benzyl ring of (η^3 -CH₂C₆H₅)Co[P(OCH₃)₃]₃ (see Table III), which suggests that the η^3 coordination of the benzyl ligand results in some degree of localization in the π -electron structure of the ring. Similar phenomena have been observed in other π -benzyl structures.^{3h,i,8,9}

Finally, we note that the coordination geometry of this pseudo-trigonal-bipyramidal structure is significantly different from that of the isoelectronic (η^3 -cyclooctenyl)Co[P(OCH₃)₃]₃

complex which better approximates a square pyramid.¹⁰

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Registry No. (η^3 -CH₂C₆H₅)Co[P(OCH₃)₃]₃, 51266-18-3.

Supplementary Material Available: Listing of observed and calculated structure factor amplitudes (11 pages). Ordering information is given on any current masthead page.

(10) Tau, K. D.; Muetterties, E. L.; Day, V. W., private communication.

Contribution from the 3M Central Research Laboratories, St. Paul, Minnesota 55101

Diketonate-Exchange Reactions of Palladium Bis(hexafluoroacetylacetonate)

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Previous research from this laboratory has outlined the extensive acid-base chemistry of palladium bis(hexafluoroacetylacetonate), Pd(F₆acac)₂.¹ The reactions of this fluorinated β -diketonate with organometallic compounds have been examined, and this paper reports those with rhodium and ruthenium hydrides. Metal hydrides were of interest because

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