paired electrons on the magnetic exchange interaction.

Examination of Table XV shows that there are only relatively small differences in *J* values between the five-coordinate and six-coordinate complexes of a given metal ion. This could result from two opposing factors. When the metal ion is moved into the plane, overlap between the metal-based $d_{x^2-y^2}$ orbitals and the oxygen-based sp^2 hybrid orbitals is increased. Since this σ framework represents the dominant pathway for the superexchange mechanism, the enhanced overlap should result in an *increase* in the antiferromagnetic interaction. On the other hand, these structural changes will result in a stronger ligand field about the metal ions, leading to an enhanced difference between the energies of the metal-based and bridging oxygen atom orbitals. This will decrease the exchange interaction. As is evident from the data, these two effects apparently cancel.

The magnetic susceptibility data for the four $[LFe_2(base)_4](BF_4)_2$ complexes substantiate the statement that an increased ligand field splitting would affect the net antiferromagnetic interaction. The two iron(II) complexes with pyridine bases (py and MeNic) as the axial ligands exhibit approximately the same magnitude of interaction, whereas the two iron(II) complexes with the stronger axial bases (Im and MeIm) exhibit the weaker net antiferromagnetic interaction.

In summary, the two offsetting factors of improved orbital overlap and increased ligand field splitting for the six-coordinate complexes lead to only a small difference in the *J* values between the five- and six-coordinate complexes of a given metal ion. What is of greater significance is that the exchange parameter does vary appreciably across the $[LM_2(py)_4](BF_4)_2$ [M = Fe(II), Co(II), and Ni(II)] series. It is likely that this variation reflects the changing number of unpaired electrons from one complex to another. In this regard it is important to note that an antiferromagnetic exchange interaction has been noted[23] for MnO, FeO, CoO, and NiO, where the Néel temperatures increase regularly from 116 to 523 K in going from MnO to NiO. Each of these compounds has a rock salt structure, and the exchange interaction occurs through linear M–O–M units. Presumably both the M–O distances and the number of unpaired electrons are important. In contrast, Sinn et al.[24] very recently came to a different conclusion. Magnetic susceptibility data were collected for a series of heterobinuclear complexes. It was concluded that the differences in *J* values could be entriely accounted for by changes in structure differences in the compounds and did *not* depend on the number of unpaired electrons. It is clear that additional work is needed.

Acknowledgment. We are grateful for support from NIH Grant HL 13652 (to D.N.H.) and NSF Grant CHE79-27141 (to R.R.G.). The National Science Foundation is to be thanked for partial funding to purchase the Syntex $P2_1$ diffractometer at the University of Illinois.

Registry No. $[LFe_2(py)_4](BF_4)_2$, 76136-05-5; $[LFe_2(MeIm)_4](BF_4)_2$, 76136-07-7; $[LFe_2(MeNic)_4](BF_4)_2$, 76156-49-5; $[LFe_2(Im)_4(BF_4)_2$, 76136-09-9; $[LCo_2(py)_4](BF_4)_2$, 76136-11-3; $[LCo_2(py)_4](ClO_4)_2$, 76136-12-4; $[LNi(py)_4](BF_4)_2$, 76136-14-6; $[LNi(py)_4](ClO_4)_2$, 76156-50-8; 1,3-diaminopropane, 109-76-2; 2,6-diformyl-4-methylphenol, 7310-95-4; LCo_2Cl_2, 47737-29-1.

Supplementary Material Available: Tables VIII–XIV (nonbonding contacts, calculated and observed magnetic susceptibility data) and listings of observed and calculated structure factors (37 pages). Ordering information is given on any current masthead page.

---

(23) Nesbet, R. K. *Phys. Rev.* **1960**, *119*, 658.
(24) O'Connor, C. J.; Freyberg, D. P.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1077.

Contribution from the Departments of Chemistry, University of Nebraska, Lincoln, Nebraska 68588,
and University of California, Berkeley, California 94720

Catalytic Hydrogenation of Aromatic Hydrocarbons. 7.[1] Chemistry and Crystal Structure of (η^3-Cyclooctenyl)cobalt(I) Tris(trimethyl phosphite)

M. R. THOMPSON, V. W. DAY,*[2] K. DAVID TAU, and E. L. MUETTERTIES*

Received September 3, 1980

The synthesis, crystal structure, and catalytic chemistry of allylcobalt(I) phosphite complex (η^3-cyclooctenyl)cobalt(I) tris(trimethyl phosphite) is described. A single-crystal X-ray diffraction study established a $P2_1/n$ space group (a = 9.361 (3) Å, b = 15.302 (5) Å, c = 18.164 (4) Å, β = 101.28 (2)°, Z = 4). Structurally, the molecule may be described as a tetragonal pyramid with a phosphite ligand at the axial site and with a basal edge spanned by the η^3-cyclooctenyl ligand. This molecule like the paradigm of this class of molecules, (η^3-allyl)cobalt tris(trimethyl phosphite), is a catalyst precursor for arene hydrogenation. Consistent with earlier observations, the substitution of bulkier phosphites (ethyl and isopropyl) for trimethyl phosphite raised the catalyst activity and lowered the catalyst lifetime.

Introduction

Allylcobalt tris(phosphite) and -(phosphine) complexes comprise a unique class of catalysts for stereoselective hydrogenation of aromatic hydrocarbons.[3,4] For some years, we have searched[5] for suitable crystals of one of these complexes for a crystallographic analysis and have finally succeeded with a special cyclic allyl derivative. Here we describe the synthesis, crystal structure, and catalytic properties of (η^3-cyclooctenyl)cobalt(I) tris(trimethyl phosphite). There is, aside from the catalytic chemistry, a special relevance of this structure to unusual and closely related allyliron structures reported by Harlow and co-workers.[6]

Experimental Section

Reagents and Solvents. All operations with air-sensitive materials were carried out in a Vacuum Atmospheres drybox under an argon atmosphere, in a conventional vacuum system or by using Schlenk techniques. Trimethyl phosphite, triethyl phosphite, and 1,5-cyclooctadiene were purchased from Aldrich Chemical Co. Inc.; triisopropyl phosphite was purchased from Strem Chemicals. Prepurified hydrogen

---

* To whom correspondence should be addressed: V.W.D., University of Nebraska; E.L.M., University of California.

(1) Paper 6 in this series: Stuhl, L. S.; Rakowski DuBois, M., Hirsekorn, F. J.; Bleeke, J. R.; Stevens, A. E.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 2405.
(2) Camille and Henry Dreyfus Teacher-Scholar.
(3) Muetterties, E. L.; Bleeke, J. R. *Acc. Chem. Res.* **1979**, *12*, 324.
(4) Bleeke, J. R.; Muetterties, E. L. *J. Am. Chem. Soc.* **1981** *103*, 556.
(5) We would have preferred to study a single crystal of η^3-C_3H_5Co complex, but all attempts yielded crystals that had poor diffraction properties.
(6) Harlow, R. L.; McKinney, R. J.; Ittel, S. D. *J. Am. Chem. Soc.* **1979**, *101*, 7496.

0020-1669/81/1320-1237$01.25/0

Table I. Hydrogenation of Benzene[a]

	reacn time, h	% benzene conversion to cyclohexanes
$C_8H_{13}Co[P(OCH_3)_3]_3$	6	4.3
	9.5	8
	24	13
$C_8H_{13}Co[P(OC_2H_5)_3]_3$	6	5.3
	24	10.5
$C_8H_{13}Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$	7	11
	24	17
	96	17

[a] Mole ratio of reactant/catalyst = 100; products were analyzed by ^1H NMR spectroscopy and by gas chromatography;[4] cyclohexane was the only detectable benzene product; cyclooctane produced in the catalyst degradation step was detected in all the reactions.

(99.95%) was obtained from Matheson Co. Anhydrous cobalt dichloride was purchased from Alfa Products.

Pyridine was purified by drying over KOH pellets for 2 days, followed by distillation from barium oxide. 1,5-Cyclooctadiene was passed down an alumina column and degassed prior to use. Tetrahydrofuran was distilled from lithium aluminum hydride, and diethyl ether and benzene were distilled from sodium benzophenone ketyl. Pentane and hexane were distilled from calcium hydride under nitrogen. The trialkyl phosphites were stored over sodium and vacuum-distilled. The commercially obtained anhydrous cobalt dichloride was redried by heating it under vacuum at 200 °C prior to use. (η^3-Cyclooctenyl)(η^4-1,5-cyclooctadiene)cobalt was prepared by a modified literature method.[7]

Physical Measurements. Proton NMR spectra were recorded on a Varian Associates A60-A or EM-390 spectrometer. Phosphorus-31 spectra were recorded on a Bruker HX-90 spectrometer, and chemical shifts were referenced to $P(OCH_3)_3$. Gas chromatographic separations were performed on a Perkin-Elmer 990 gas chromatograph with a flame ionization detector using a 12 ft × $^1/_8$ in. 15% OV-17 Chromosorb W column. Microanalyses were done by Pascher Mikroanalytisches Laboratorium, Bonn, Germany.

General Procedure for Catalytic Hydrogenations. See the procedure described by Stuhl et al.[1] Results are presented in Table I.

$C_8H_{13}Co[P(OCH_3)_3]_3$. To a solution of $C_8H_{13}Co(1,5\text{-}C_8H_{12})$ (0.835 g, 3.02 mmol) in pentane (25 mL) was added $P(OCH_3)_3$ (1.875 g in 5 mL of pentane, 15.11 mmol). After standing for ~16 h, the solution was concentrated to ~10 mL on a rotary evaporator. Orange-red crystals were collected by filtration, washed with a small amount of pentane, and vacuum-dried. Another crop of crystals were obtained by cooling the filtrate to −40 °C (1 g, 61% yield; mp 119 °C dec). Crystals of X-ray quality were obtained by recrystallization from a pentane–diethyl ether solution. Anal. Calcd for $C_{17}H_{40}CoO_9P_3$: C, 37.78; H, 7.48; P, 17.19. Found: C, 37.99; H, 7.47; P, 17.48. ^1H NMR (benzene-d_6, 90 MHz, 30 °C): δ 0.50–2.90 (br m, 10), 3.00–3.50 (br m partly obscured by the phosphite CH_3 resonance, 2), 3.53 ("filled-in" d, 27), 5.23 (t of quar, 1). $^{31}P\{^1H\}$ NMR (acetone-d_6, −78 °C): one broad singlet at 29.07 ppm (downfield from $P(OCH_3)_3$.

$C_8H_{13}Co[P(OC_2H_5)_3]_3$. This compound was prepared by the procedure described above for the methyl analogue. The reaction solution was vacuum-concentrated to an orange-brown residue. The residue was redissolved in a minimum amount of pentane, and the solution was cooled to −40 °C. Orange-brown crystals were collected by filtration and were vacuum-dried (37% yield; mp 141 °C dec). Anal. Calcd for $C_{26}H_{58}CoO_9P_3$: C, 46.84; H, 8.79; P, 13.94. Found: C, 47.08, H, 8.80; P, 13.85. ^1H NMR (benzene-d_6, 90 MHz, 30 °C): δ 0.30–0.95 (m, 2), 1.20 (t, 27), 1.40–2.50 (m, 8, partially obscured by phosphite CH_3 resonance), 3.00–3.75 (m, 2, partially obscured by phosphite resonance), 4.02 (m, 18), 5.20 (m, 1). $^{31}P\{^1H\}$ NMR (A_3 spectrum down to −90 °C): δ ~29.

$C_8H_{13}Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$. This compound was prepared and isolated by the procedure described for the methyl analogue (47% yield; mp 155 °C dec). Anal. Calcd for $C_{35}H_{76}CoO_9P_3$: C, 53.01; H, 9.68; P, 11.72. Found: C, 52.74; H, 9.83; P, 12.33. ^1H NMR (benzene-d_6, 90 MHz, 30 °C): δ 0.50–1.00 (m), 1.28 (d, 54, J = 6 Hz), 1.50–2.35 (br m), 3.00 (br), 4.85 (m).

Crystallography. Single crystals of $(\eta^3\text{-}C_8H_{13})Co[P(OCH_3)_3]_3$ were at 20 ± 1 °C monoclinic space group $P2_1/n$ (a special setting of $P2_1/c\text{-}C_{2h}^5$, No. 14)[8] with a = 9.361 (3) Å, b = 15.302 (5) Å, c = 18.164 (4) Å, β = 101.28 (2)°, Z = 4, and d(calcd) = 1.408 g/cm³. A nearly cube-shaped specimen, 0.50 mm on an edge, was glued under nitrogen to the inside of a thin-walled glass capillary. This capillary was sealed, and the crystal was then accurately centered optically on a computer-controlled four-circle Syntex P_1 autodiffractometer. Intensity measurements utilized graphite-monochromated Mo K$\bar{\alpha}$ radiation and the ω-scanning technique with a 4° takeoff angle and a normal-focus X-ray tube.[9] A total of 5887 independent reflections having $2\theta_{Mo\,K\bar{\alpha}} < 55°$ were measured in concentric shells of increasing 2θ containing approximately 2950 reflections each. The six standard reflections, measured every 300 reflections, gave no indication of possible disalignment and/or deterioration of the crystal.

Of the 5887 reflections examined,[11] 1929 were eventually rejected as objectively unobserved,[13] having $I < 3\sigma(I)$. The heavy-atom technique, difference Fourier syntheses, and full-matrix least-squares refinement were used with the remaining 3958 observed intensities in the determination and refinement of the structure. Structure factor calculations employed the atomic form factors compiled by Cromer and Mann,[14] an anomalous dispersion correction to the scattering factor of the cobalt and phosphorus atoms,[15] and a least-squares refinable extinction correction.[16] Anisotropic refinement gave R_1 = 0.054 and R_2 = 0.060 for 2397 reflections having $2\theta_{Mo\,K\bar{\alpha}} < 43°$ and $I > 3\sigma(I)$. A difference Fourier synthesis calculated at this point contained electron density maxima at locations corresponding to chemically anticipated positions of the 40 independent hydrogen atoms. Further unit-weighted least-squares minimization of the function $\sum w(|F_o| - K|F_c|)^2$ with these low-angle data which employed anisotropic thermal parameters for nonhydrogen atoms and isotropic thermal parameters for hydrogen atoms gave R_1 = 0.027 and R_2 = 0.027 for 2397 reflections. At this point the more complete ($2\theta_{Mo\,K\bar{\alpha}} \leq 55°$) data set was included, and unit-weighted refinement for the 70 atoms of the asymmetric unit gave R_1 = 0.033 and R_2 = 0.033 for the 3958 independent reflections having $2\theta_{Mo\,K\bar{\alpha}} \leq 55°$ and $I > 3\sigma(I)$. Empirical weights ($w = 1/\sigma^2$) were then calculated[17] with the a_n coefficients derived from the least-squares fitting of the curve $||F_o| - |F_c|| = \sum_0^4 a_n|F_o|^n$ where the F_c values were calculated from the fully refined model using unit weighting.

Results and Discussion

Synthesis of (η^3-cyclooctenyl)cobalt tris(trimethyl phosphite)

---

(7) Rossi, M.; Sacco, A. *J. Chem. Soc. Chem. Commun.* **1969**, 471.

(8) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1969; Vol. 1, p 99.

(9) For details of data collection see ref 10.

(10) Wreford, S. S.; Kouba, J. K.; Kirner, J. F.; Muetterties, E. L.; Tavanaiepour, I.; Day, V. W. *J. Am. Chem. Soc.* **1980**, *102*, 1558.

(11) The linear absorption coefficient of the crystal for Mo K$\bar{\alpha}$ radiation[12] was 0.93 mm^{-1}, yielding a μr of 0.29 for a spherical crystal having the same volume as the cube-shaped specimen actually used. No absorption corrections were made, and the intensities were reduced to relative square amplitudes, $|F_o|^2$, by means of standard Lorentz and polarization corrections.

(12) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1968; Vol. III, p 166.

(13) See ref 10 for rejection criterion.

(14) Cromer, D. T.; Mann, J. L. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(15) Cromer, D. T. *Acta Crystallogr.* **1965**, *18*, 17.

(16) Zachariasen, W. H. *Acta Crystallogr.* **1967**, *23*, 558.

(17) From $\sigma = \sum_0^4 a_m|F_o|^n = 0.930 - 1.31 \times 10^{-2}|F_o| + 2.29 \times 10^{-4}|F_o|^2 - 7.13 \times 10^{-7}|F_o|^3$. The final cycles of full-matrix least-squares refinement utilized these weights to give final values of R_1 = 0.033 and R_2 = 0.035 for 3958 independent reflections having $2\theta_{Mo\,K\bar{\alpha}} < 55°$ and $I > 3\sigma(I)$. During the final cycle of refinement, no parameter (including those of hydrogen atoms) shifted by more than $0.29\sigma_p$ with the average shift being $0.02\sigma_p$, where σ_p is the estimated standard deviation of the parameter.[18,19]

(18) See paragraph at end of paper regarding supplementary material.

(19) The following programs were used on IBM 360/65 or 370/158 computers for this work: MAGTAP, SCALEUP, and SCTFT4, data reduction programs written in this laboratory by V. W. Day; FORDAP, Fourier and Patterson synthesis program; ORFLSE, full-matrix least-squares structure refinement program, a highly modified version of Busing, Martin, and Levy's original ORFLS; ORFFE, bond length and angles with standard deviations by Busing, Martin, and Levy; ORTEP2, thermal ellipsoid plotting program by Johnson; MPLANE, least-squares mean plane calculation program from L. Dahl's group.

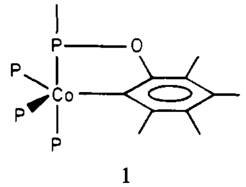
Table II. Atomic Coordinates in Crystalline $(\eta^3\text{-}C_8H_{13})Co(P(OCH_3)_3)_3$[a]

atom type[b]	fractional coordinates				atom type[b]	fractional coordinates			
	10^5x	10^5y	10^5z	B,[c] Å^2		10^5x	10^5y	10^5z	B,[c] Å^2
Co	5443 (4)	34 287 (2)	29 640 (2)	2.7	P_2	26093 (8)	39 391 (5)	34 876 (4)	3.2
P_1	−7333 (8)	45 591 (6)	26 668 (4)	3.7	P_3	7467 (8)	30574 (5)	18 638 (4)	3.7

atom type[b]	fractional coordinates				atom type[b]	fractional coordinates			
	10^4x	10^4y	10^4z	B,[c] Å^2		10^4x	10^4y	10^4z	B,[c] Å^2
O_{11}	−2419 (3)	4491 (2)	2285 (2)	5.7	H_{61}	−54 (4)	110 (2)	508 (2)	4 (1)
O_{12}	−145 (3)	5281 (2)	2161 (1)	5.5	H_{62}	−109 (4)	148 (2)	427 (2)	4 (1)
O_{13}	−965 (3)	5151 (2)	3368 (1)	5.3	H_{71}	31 (5)	239 (3)	558 (3)	6 (1)
O_{21}	2949 (2)	4272 (2)	4358 (1)	4.7	H_{72}	−134 (5)	249 (3)	515 (2)	5 (1)
O_{22}	3293 (3)	4797 (2)	3166 (1)	4.8	H_{81}	−17 (4)	369 (3)	486 (2)	4 (1)
O_{23}	3926 (2)	3253 (1)	3577 (1)	4.2	H_{82}	114 (3)	320 (2)	468 (2)	2 (1)
O_{31}	−274 (3)	2236 (2)	1562 (1)	4.5	H_{111}	−261 (5)	332 (3)	181 (3)	6 (1)
O_{32}	316 (3)	3762 (2)	1207 (1)	4.9	H_{112}	−397 (6)	385 (3)	165 (3)	7 (1)
O_{33}	2276 (2)	2769 (1)	1648 (1)	4.4	H_{113}	−270 (8)	418 (5)	141 (4)	14 (3)
C_{11}	−3046 (5)	3800 (4)	1826 (3)	6.4	H_{121}	−130 (7)	541 (4)	128 (3)	8 (2)
C_{12}	−894 (8)	5778 (5)	1568 (3)	8.0	H_{122}	−187 (6)	582 (4)	162 (3)	8 (2)
C_{13}	−1897 (6)	5883 (3)	3326 (3)	6.5	H_{123}	−34 (7)	611 (5)	133 (4)	12 (2)
C_{21}	2192 (6)	5014 (3)	4566 (3)	5.6	H_{131}	−277 (4)	572 (2)	308 (2)	3 (1)
C_{22}	3424 (5)	4812 (3)	2383 (2)	5.5	H_{132}	−180 (7)	624 (4)	289 (4)	11 (2)
C_{23}	5411 (4)	3492 (4)	3870 (3)	5.8	H_{133}	−173 (6)	614 (4)	381 (4)	10 (2)
C_{31}	−280 (6)	1811 (4)	857 (3)	6.1	H_{211}	247 (5)	552 (3)	442 (3)	6 (1)
C_{32}	913 (10)	3876 (4)	565 (4)	7.3	H_{212}	234 (5)	502 (3)	508 (3)	6 (1)
C_{33}	3126 (5)	2075 (3)	2032 (3)	5.2	H_{213}	119 (6)	498 (3)	434 (3)	8 (1)
C_1	−686 (3)	3201 (3)	3811 (2)	4.2	H_{221}	246 (6)	500 (3)	206 (3)	8 (1)
C_2	−651 (3)	2519 (2)	3304 (2)	3.9	H_{222}	369 (4)	419 (3)	247 (2)	5 (1)
C_3	685 (4)	2102 (2)	3292 (2)	3.8	H_{223}	417 (4)	519 (3)	237 (2)	5 (1)
C_4	1755 (4)	1818 (2)	3986 (2)	4.4	H_{231}	547 (5)	387 (3)	431 (3)	7 (1)
C_5	1105 (5)	1203 (3)	4504 (2)	5.6	H_{232}	585 (5)	304 (3)	409 (3)	6 (1)
C_6	−287 (5)	1500 (3)	4728 (2)	5.4	H_{233}	576 (6)	392 (4)	355 (3)	10 (2)
C_7	−353 (5)	2387 (3)	5074 (2)	5.5	H_{311}	56 (5)	191 (3)	70 (3)	6 (1)
C_8	61 (5)	3178 (2)	4633 (2)	4.6	H_{312}	−102 (6)	207 (3)	53 (3)	8 (2)
H_1	−157 (4)	348 (2)	372 (2)	3 (1)	H_{313}	−38 (6)	125 (4)	91 (3)	9 (2)
H_2	−144 (4)	238 (2)	292 (2)	3 (1)	H_{321}	102 (10)	333 (6)	33 (5)	17 (3)
H_3	65 (4)	170 (2)	293 (2)	3 (1)	H_{322}	134 (7)	436 (4)	65 (4)	10 (2)
H_{41}	257 (2)	153 (2)	384 (2)	3 (1)	H_{323}	45 (6)	415 (5)	24 (3)	9 (2)
H_{42}	220 (3)	229 (2)	427 (2)	1 (1)	H_{331}	332 (4)	210 (2)	254 (2)	3 (1)
H_{51}	183 (4)	115 (2)	497 (2)	4 (1)	H_{332}	392 (5)	207 (3)	185 (3)	7 (1)
H_{52}	98 (5)	64 (3)	426 (2)	5 (1)	H_{333}	256 (6)	155 (4)	190 (3)	8 (2)

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms are labeled in agreement with Figure 1. [c] For nonhydrogen atoms which are modeled with anisotropic thermal parameters of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$, this is the equivalent isotropic thermal parameter calculated from $B = 4[V^2 \det(\beta_{ij})]^{1/3}$; for hydrogen atoms it is the isotropic temperature factor.

and the analogues based on ethyl and isopropyl phosphites was most easily effected by direct reaction of the respective phosphites with (η^3-cyclooctenyl)cobalt η^4-1,5-cyclooctadiene to give 40–60% yields of purified product. There was no evidence of hydride formation in these reactions contrary to implications in earlier reports;[7] however, as established by Gosser,[20] the triaryl phosphites behave in different fashion and form a hydride by internal oxidative addition of an aryl ortho C–H bond to the cobalt center to ultimately give **1**.



1

All the trialkyl phosphite derivatives of η^3-cyclooctenylcobalt were active catalysts for benzene hydrogenation. The trimethyl phosphite complex had a catalytic activity comparable to that[1] of $(\eta^3\text{-}C_3H_5)Co[P(OCH_3)_3]_3$. Consistent with earlier observations, replacement of the trimethyl phosphite by a bulkier phosphite raised the catalytic activity of the (η^3-cyclooctenyl)cobalt complex but not to the same high levels observed in $(\eta^3\text{-}C_3H_5)Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$. Also consistent with the earlier studies, these substitutions led to lower catalyst lifetimes. The scientifically redeeming features of the cyclooctenylcobalt complexes were (i) their utility in mechanistic studies[4] whereby the true catalyst precursor was established and (ii) their crystal quality. Single crystals with excellent diffractive properties were easily obtained from ether–pentane solutions.

Solid-State Structure of $(\eta^3\text{-}C_8H_{13})Co[P(OCH_3)_3]_3$. Final atomic coordinates and (equivalent) isotropic thermal parameters for the X-ray structural analysis of $(\eta^3\text{-}C_8H_{13})Co(P(OCH_3)_3)_3$ (**2**) are presented in Table II; anisotropic thermal parameters for nonhydrogen atoms of **2** are given in Table III (supplementary material).[8] A perspective model of the cobalt structure is presented in Figure 1.[21] Covalent bond lengths and angles for **2** are listed with their estimated standard deviations in Tables IV–VI.[18] These parameters are totally

---

(20) Gosser, L. W. *Inorg. Chem.* **1975**, *14*, 1453.

(21) The numbering scheme used to designate atoms of **2** is as follows. Carbon atoms of the cyclooctenyl ligand carry a single numerical subscript. Atoms for a particular phosphite ligand are distinguished from those of other phosphites by a first numerical subscript to the appropriate atomic symbol. Phosphite oxygen and carbon atoms carry a second numerical subscript to distinguish between different methoxy arms of the same ligand. Hydrogen atoms have the same numerical subscripts as the carbon atoms to which they are covalently bonded and an additional numerical subscript whenever more than one hydrogen is bonded to the same atom.

Table IV. Covalent Bond Lengths in Crystalline $(\eta^3\text{-}C_8H_{13})Co(P(OCH_3)_3)_3$[a]

type[b]	length, Å	
$Co-P_1$	2.112 (1)	2.117 (1, 5, 5, 2)[c]
$Co-P_3$	2.122 (1)	
$Co-P_2$	2.129 (1)	
$Co-C_1$	2.125 (3)	2.119 (3, 6, 6, 2)
$Co-C_3$	2.113 (3)	
$Co-C_2$	1.960 (3)	
$Co-C_a$[d]	1.785	
P_1-O_{11}	1.598 (2)	1.610 (2, 9, 21, 9)
P_1-O_{12}	1.601 (3)	
P_1-O_{13}	1.612 (3)	
P_2-O_{21}	1.631 (2)	
P_2-O_{22}	1.619 (2)	
P_2-O_{23}	1.602 (2)	
P_3-O_{31}	1.609 (2)	
P_3-O_{32}	1.600 (2)	
P_3-O_{33}	1.617 (2)	
$O_{11}-C_{11}$	1.402 (5)	1.420 (5, 16, 31, 9)
$O_{12}-C_{12}$	1.391 (5)	
$O_{13}-C_{13}$	1.413 (5)	
$O_{21}-C_{21}$	1.428 (5)	
$O_{22}-C_{22}$	1.451 (5)	
$O_{23}-C_{23}$	1.435 (4)	
$O_{31}-C_{31}$	1.434 (4)	
$O_{32}-C_{32}$	1.399 (5)	
$O_{33}-C_{32}$	1.423 (4)	
C_1-C_2	1.397 (5)	1.403 (5, 6, 6, 2)
C_2-C_3	1.408 (5)	
C_3-C_4	1.511 (5)	1.515 (5, 4, 4, 2)
C_1-C_8	1.519 (5)	
C_4-C_5	1.538 (5)	1.523 (6, 17, 20, 4)
C_5-C_6	1.509 (6)	
C_6-C_7	1.503 (6)	
C_7-C_8	1.542 (5)	

type[b]	length, Å	
C_1-H_1	0.91 (3)	0.93 (5, 5, 15, 40)
C_2-H_2	0.94 (4)	
C_3-H_3	0.90 (3)	
C_4-H_{41}	0.96 (4)	
C_4-H_{42}	0.94 (3)	
C_5-H_{51}	0.97 (4)	
C_5-H_{52}	0.97 (4)	
C_6-H_{61}	0.95 (4)	
C_6-H_{62}	1.01 (4)	
C_7-H_{71}	1.01 (5)	
C_7-H_{72}	0.97 (4)	
C_8-H_{81}	0.93 (3)	
C_8-H_{82}	1.00 (4)	
$C_{11}-H_{111}$	0.85 (5)	
$C_{11}-H_{112}$	0.86 (5)	
$C_{11}-H_{113}$	1.06 (8)	
$C_{12}-H_{121}$	0.81 (6)	
$C_{12}-H_{122}$	0.94 (5)	
$C_{12}-H_{123}$	0.89 (5)	
$C_{13}-H_{131}$	0.89 (3)	
$C_{13}-H_{132}$	0.98 (6)	
$C_{13}-H_{133}$	0.94 (6)	
$C_{21}-H_{211}$	0.89 (5)	
$C_{21}-H_{212}$	0.91 (5)	
$C_{21}-H_{213}$	0.95 (6)	
$C_{22}-H_{221}$	1.02 (5)	
$C_{22}-H_{222}$	0.99 (4)	
$C_{22}-H_{223}$	0.91 (4)	
$C_{23}-H_{231}$	0.98 (6)	
$C_{23}-H_{232}$	0.86 (5)	
$C_{23}-H_{233}$	0.97 (5)	
$C_{31}-H_{311}$	0.90 (5)	
$C_{31}-H_{312}$	0.91 (5)	
$C_{31}-H_{313}$	0.87 (6)	
$C_{32}-H_{321}$	0.95 (6)	
$C_{32}-H_{322}$	0.83 (6)	
$C_{32}-H_{323}$	0.78 (6)	
$C_{33}-H_{331}$	0.91 (5)	
$C_{33}-H_{332}$	0.87 (5)	
$C_{33}-H_{333}$	0.97 (5)	

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms labeled in agreement with Figure 1 and Tables I and II. [c] All average values; see ref 27.

consistent with the formulation of **2** as an 18-electron species which contains three σ-bonded phosphite ligands and a π-bonded allylic ligand. The overall structure of **2** resembles closely that recently reported[22] for $(\eta^3\text{-}C_3H_5)Co(CO)_2[P(C_6H_5)_3]$, is presumably quite similar to that of $(\eta^3\text{-}C_3H_5)Co[P(OCH_3)_3]_3$,[1,5] and is quite different from $(\eta^3\text{-benzyl})Co[P(OCH_3)_3]_3$.[23] It represents another member of a structurally interesting series of $(\eta^3\text{-}C_8H_{13})M(P(OCH_3)_3)_3$ complexes. Other members of this latter series are electron-deficient iron complexes which exhibit significant bonding interactions between the metal and a cyclooctenyl hydrogen atom as in $(\eta^3\text{-}C_8H_{13})Fe[P(OCH_3)_3]_3^+$[6,24] and neutral $(\eta^3\text{-}C_8H_{13})Fe[P(OCH_3)_3]_3$.[6]

If the cyclooctenyl ligand is considered to occupy a single coordination site, the Co(I) coordination geometry in **2** should best be described as *pseudo*tetrahedral.[25] However, all allylmetal structures with four or less other ligating atoms in the coordination sphere are best geometrically described in the

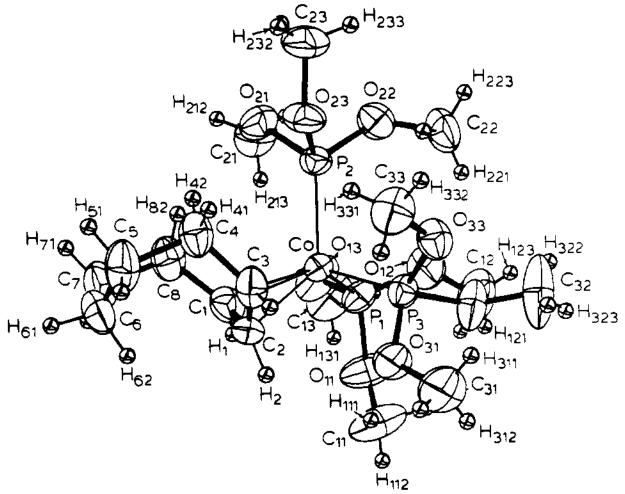


Figure 1. ORTEP drawing of the solid-state structure of $(\eta^3\text{-}C_8H_{13})Co[P(OCH_3)_3]_3$ (**2**). All nonhydrogen atoms are represented by thermal vibration ellipsoids drawn to encompass 50% of the electron density; hydrogen atoms are represented by arbitrarily small spheres for purposes of clarity. The labeling scheme is described in ref 21; atoms H_3, H_{52}, H_{72}, H_{113}, H_{122}, H_{132}, H_{133}, H_{211}, H_{222}, H_{231}, H_{313}, H_{321}, and H_{333} are not labeled in this drawing. Atom H_{81} is hidden from view.

---

(22) Rinze, P. V.; Muller, U. *Chem. Ber.* **1979**, *112*, 1973.

(23) Bleeke, J. R.; Burch, R. R.; Coulman, C. L.; Schardt, B. C., submitted for publication in *Inorg. Chem.*

(24) Williams, J. M.; Brown, R. K.; Schultz, A. J.; Stucky, G. D.; Ittel, S. D. *J. Am. Chem. Soc.* **1978**, *100*, 7407.

(25) Five of the six angles subtended at Co by the three phosphorus atoms and the allylic center of gravity (C_a) are consistent with such a description. Steric factors should produce two sets of equivalent "tetrahedral" L–Co–L angles in **2**: the three C_a–Co–P angles should be nearly equal with a value greater than that of an idealized tetrahedron (109.5°), and the three P–Co–P angles should all be equal but less than 109.5°. As the data in Table V indicate, the C_a–Co–P angles in **2** are equivalent (average = 115.8°) and ~6° larger than the tetrahedral value.

Table V. Bond Angles for Nonhydrogen Atoms in Crystalline $(\eta^3\text{-}C_8H_{13})Co(P(OCH_3)_3)_3$[a]

type[b]q	angle, deg	
P_1CoP_2	103.5 (1)	104.9 (1, 14, 14, 2)[d]
P_2CoP_3	106.2 (1)	
C_aCoP_2[c]	116.5	
P_1CoP_3	97.4 (1)	
C_aCoP_1[c]	116.4	115.4 (..., 10, 10, 2)
C_aCoP_3[c]	114.4	
C_1CoC_2	39.7 (1)	40.0 (1, 3, 3, 2)
C_2CoC_3	40.2 (1)	
C_1CoC_3	69.6 (1)	
P_2CoC_1	108.1 (1)	105.6 (1, 26, 26, 2)
P_2CoC_3	103.0 (1)	
P_2CoC_2	130.1 (1)	
P_1CoC_1	87.7 (1)	88.8 (1, 10, 10, 2)
P_3CoC_3	89.8 (1)	
P_1CoC_3	149.3 (1)	146.2 (1, 31, 31, 2)
P_3CoC_1	143.1 (1)	
CoC_1C_8	120.3 (2)	120.4 (2, 1, 1, 2)
$C_5C_3C_4$	120.4 (2)	

type[b]	angle, deg	
CoP_1O_{11}	120.3 (1)	118.3 (1, 32, 63, 9)
CoP_1O_{12}	118.1 (1)	
CoP_1O_{13}	114.5 (1)	
CoP_2O_{21}	122.4 (1)	
CoP_2O_{22}	121.7 (1)	
CoP_2O_{23}	114.7 (1)	
CoP_3O_{31}	112.0 (1)	
CoP_3O_{32}	117.8 (1)	
CoP_3O_{33}	123.2 (1)	
$P_1O_{11}C_{11}$	124.7 (3)	123.9 (3, 29, 61, 9)
$P_1O_{12}C_{12}$	130.0 (4)	
$P_1O_{13}C_{13}$	125.4 (3)	
$P_2O_{21}C_{21}$	119.5 (2)	
$P_2O_{22}C_{22}$	118.8 (2)	
$P_2O_{23}C_{23}$	122.8 (3)	
$P_3O_{31}C_{31}$	123.8 (3)	
$P_3O_{32}C_{32}$	128.4 (3)	
$P_3O_{33}C_{33}$	121.4 (2)	
$C_8C_1C_2$	124.4 (3)	124.4 (3, 1, 1, 2)
$C_2C_3C_4$	124.3 (3)	
$C_1C_2C_3$	119.0 (3)	
$C_3C_4C_5$	114.3 (3)	116.4 (3, 16, 32, 5)
$C_4C_5C_6$	116.5 (3)	
$C_5C_6C_7$	119.6 (4)	
$C_6C_7C_8$	117.2 (3)	
$C_7C_8C_1$	114.5 (3)	

[a] Figures in parentheses are the estimated standard deviations in the last significant digit. [b] Atoms labeled in agreement with Figure 1 and Tables I-III. [c] C_a is center of gravity for the allyl ligand. [d] All average values; see ref 27.

context of a polyhedron (or polygon) in which the allyl ligand takes up two coordination sites.[26] In addition, the striking inequality in the P–Co–P angles clearly shows that an idealized tetrahedral representation is not appropriate; the angles are 103.5 (1), 106.2 (1) and 97.4 (1)° (Table V).[27] These P–Co–P angles identify a square pyramid as a better idealized representation of this allylcobalt structure with the allylic fragment occupying two adjacent basal coordination sites. The four "basal" atoms (P_1, P_3, C_1, and C_3) in **2** are coplanar[28] to within 0.08 Å, and Co is displaced by 0.55 Å from their least-squares mean plane toward P_2. The maximum possible symmetry of C_s-*m* for such a "square-pyramidal" species is approximated rather closely in **2**; the mirror plane would ideally contain Co, C_a,[25] C_2, C_6, H_{61}, and P_2 and the carbon, the oxygen, and a hydrogen atom for one of the P_2 methoxy arms. Co, C_a,[25] C_2, C_6, H_{61}, H_{62}, and P_2 are all coplanar[29] to within 0.05 Å, and their least-squares mean plane intersects that of the "square base" in a dihedral angle of 92.0°. The three-carbon allylic grouping[30] intersects these mean planes in dihedral angles of 90.8 and 101.4°. The allylic C_1–C_2–C_3 grouping in **2** has a staggered orientation with respect to the $P_1 \cdots P_2 \cdots P_3$ face (i.e., the nonallylic portion of the cyclooctenyl ring is above the basal plane). A similar orientation has been observed for the allyl ligand in $\eta^3\text{-}C_3H_5Co(CO)_2[P(C_6H_5)_3]$ and is the one shown[6,26] to be most stable for 18-electron $(\eta^3\text{-allyl})ML_3$ systems.

The structure of **2** is qualitatively different from that of $(\eta^3\text{-benzyl})Co[P(OCH_3)_3]_3$,[23] a fact that is fully explicable. Although an η^3-benzyl ligand is formally analogous to an η^3-allyl ligand, the precise electronic, and accordingly structural, analogy does not prevail because, unlike the allyl radical (or ion), the benzyl radical (or ion) has a significant variation in electron density over the three carbon atoms involved in η^3-allyl or η^3-benzyl interactions with a metal center.

Acknowledgment. This research was supported through a grant from the National Science Foundation (E.L.M.) and from the University of Nebraska Computer Center.

Registry No. **2**, 76430-71-2; $C_8H_{13}Co[P(OC_2H_5)_3]_3$, 76430-72-3; $C_8H_{13}Co[P(O\text{-}i\text{-}C_3H_7)_3]_3$, 76430-73-4; $C_8H_{13}Co(1,5\text{-}C_8H_{12})$, 34829-55-5.

Supplementary Material Available: A listing of structure factors, Table III, anisotropic thermal parameters, and Table VI, bond angles for **2** (20 pages). Ordering information is given on any current masthead page.

---

(26) Putnik, C. F.; Welter, J. J.; Stucky, G. D.; D'Aniello, M. J., Jr.; Sosinsky, B. A.; Kirner, J. F.; Muetterties, E. L. *J. Am. Chem. Soc.* **1978**, *100*, 4107.

(27) The first number in parentheses following an averaged value for a bond length or angle 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 average value, respectively; the fourth number is the number of individual values included in the average.

(28) The plane is defined by the equation $0.815X + 0.368Y + 0.448Z = 3.298$, where X, Y, and Z are orthogonal coordinates along $\vec{a}$, $\vec{b}$, and $\vec{c}^*$, respectively, of the crystal system.

(29) Mean plane defined by $-0.581X + 0.714Y + 0.392Z = 6.075$.

(30) Mean plane defined by $-0.322X - 0.656Y + 0.682Z = 2.061$.