

Synthesis, Structure, and Solution Dynamics of (η^5 -2,4-Dimethylpentadienyl)Co[P(C₂H₅)₃]₂ and (*anti*- η^3 -2,4-Dimethylpentadienyl)Co[P(CH₃)₃]₃

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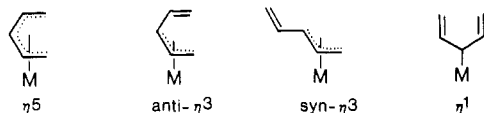
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Reaction of CoCl₂ with P(C₂H₅)₃, potassium 2,4-dimethylpentadienide, and a reducing agent (zinc dust or additional potassium 2,4-dimethylpentadienide) results in the formation of (η^5 -2,4-dimethylpentadienyl)Co[P(C₂H₅)₃]₂, **1**. The crystal structure of **1** has been determined by X-ray diffraction. The complex crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 7.928 (2) Å, *b* = 18.041 (7) Å, *c* = 15.592 (4) Å, β = 92.81 (2)°, and *Z* = 4. The two P(C₂H₅)₃ ligands in **1** are oriented with one eclipsing the open edge and the other eclipsing the central carbon atom of the 2,4-dimethylpentadienyl ligand. The five cobalt-bound carbon atoms of the U-shaped 2,4-dimethylpentadienyl ligand are essentially coplanar. Reaction of ClCo[P(CH₃)₃]₃ with potassium 2,4-dimethylpentadienide produces (*anti*- η^3 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₃, **2a**. The crystal structure of **2a** has been determined by X-ray diffraction. The complex crystallizes in the monoclinic space group *P*2₁/*c* with *a* = 8.927 (2) Å, *b* = 15.008 (6) Å, *c* = 16.694 (4) Å, β = 104.33 (2)°, and *Z* = 4. The geometry about the cobalt atom approximates a square pyramid, with two of the allylic carbon atoms of the 2,4-dimethylpentadienyl ligand (C1 and C3) occupying adjacent basal sites, two of the P(CH₃)₃ phosphorus atoms (P1 and P2) occupying the remaining basal sites, and the final P(CH₃)₃ phosphorus atom (P3) residing in the axial site. The mouth of the allylic portion of the 2,4-dimethylpentadienyl ligand faces the axial P(CH₃)₃ ligand; as a result, the vinylic portion of the 2,4-dimethylpentadienyl ligand lies above the basal plane. The 2,4-dimethylpentadienyl ligand is U-shaped. However, it is *not* planar; the vinylic moiety is bent substantially out of the plane of the allylic moiety away from the cobalt atom. In solution, **2a** equilibrates with its *syn* isomer, (*syn*- η^3 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₃, **2b**, producing a 70:30 mixture of **2a**-**2b**. Spin saturation transfer NMR experiments suggest that the mechanism for interconversion of **2a** and **2b** involves a C3-bound (η^1 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₃ intermediate.

Introduction

Although cyclopentadienylmetal complexes are ubiquitous in organotransition-metal chemistry, the synthesis and reactivity of metal complexes possessing acyclic pentadienyl ligands have remained largely unexplored.^{1,2} We anticipate that pentadienylmetal complexes will, in general, possess a rich reaction chemistry because the pentadienyl ligand can potentially bond to a metal center in a variety of energetically accessible modes.³



We now report the syntheses and X-ray crystal structures of two new pentadienylcobalt complexes (η^5 -2,4-dimethylpentadienyl)Co[P(C₂H₅)₃]₂, **1**, and (*anti*- η^3 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₃, **2a**. In solution, **2a** equilibrates with its *syn* isomer (*syn*- η^3 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₃, **2b**. We propose a mechanism for this process based on spin saturation transfer NMR experiments.

(1) An important contribution to this area has recently been made by Ernst, who has synthesized a series of "open metallocenes", i.e., metallocene analogues possessing two η^5 -acyclic pentadienyl ligands: Wilson, D. R.; DiLullo, A. A.; Ernst, R. D. *J. Am. Chem. Soc.* 1980, 102, 5928. Wilson, D. R.; Liu, J.-Z.; Ernst, R. D. *Ibid.* 1982, 104, 1120. Liu, J.-Z.; Ernst, R. D. *Ibid.* 1982, 104, 3737.

(2) Other reports of pentadienylmetal complexes include the following: (a) Mahler, J. E.; Pettit, R. *J. Am. Chem. Soc.* 1962, 84, 1511. (b) Giannini, U.; Pellino, E.; Lachi, M. P. *J. Organomet. Chem.* 1968, 12, 551. (c) Seyferth, D.; Goldman, E. W.; Pomet, J. *Ibid.* 1981, 208, 189. (d) Ernst, R. D.; Cymbaluk, T. H. *Organometallics* 1982, 1, 708. (e) Bleeke, J. R.; Hays, M. K. *Ibid.* 1984, 3, 506.

(3) As a case in point, we have recently reported a stereospecific manganese-centered pentadienyl coupling reaction that apparently proceeds through bis(*anti*- η^3 -pentadienyl)Mn(PR₃)₂ and bis(*syn*- η^3 -pentadienyl)Mn(PR₃)₂ intermediates: Bleeke, J. R.; Kotyk, J. J. *Organometallics* 1983, 2, 1263.

Experimental Section

A. General Comments. All manipulations were carried out under inert atmosphere, using either drybox or Schlenk techniques. Diethyl ether and tetrahydrofuran were dried with sodium/benzophenone and distilled before use. Pentane was dried over calcium hydride and distilled. Trimethylphosphine and triethylphosphine were obtained from Strem Chemicals; 2,4-dimethylpentadiene was purchased from Wiley Organics. All were used without further purification. All NMR experiments except the spin saturation transfer experiments were performed on a JEOL FX-100 NMR spectrometer. The spin saturation transfer experiments were carried out on a Nicolet NT360 NMR spectrometer at the University of Illinois—Champaign/Urbana. ¹H and ¹³C NMR spectra are referenced to tetramethylsilane. ³¹P NMR spectra are referenced to trimethylphosphine or triethylphosphine, as indicated. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

B. Synthesis of (η^5 -2,4-Dimethylpentadienyl)Co[P(C₂H₅)₃]₂, **1.** **Method 1.** A 50-mL sample of tetrahydrofuran was added to CoCl₂ (1.3 g, 0.010 mol), producing a light blue solution with some undissolved CoCl₂. Triethylphosphine (2.4 g, 0.020 mol) was added, and the resulting dark blue solution was stirred until none of the solid CoCl₂ remained. Excess zinc dust (2.0 g, 0.031 mol) was added, and the reaction flask was cooled to 0 °C. Potassium 2,4-dimethylpentadienide-tetrahydrofuran⁴ (2.1 g, 0.010 mol) in 70 mL of tetrahydrofuran was added dropwise with stirring, yielding a brown solution. The solution was warmed to room temperature, stirred for 24 h, filtered, and evaporated to dryness. The brown product was extracted with pentane and crystallized from a saturated pentane solution at -30 °C; yield of crystalline product 1.6 g (41%).

Method 2. The same procedure as above was followed, except the zinc dust was replaced with a second equivalent of potassium 2,4-dimethylpentadienide-tetrahydrofuran (total KC₇H₁₁-OC₄H₉ = 4.1 g, 0.020 mol); yield of crystalline product 2.3 g (59%). ¹H

(4) Yasuda, H.; Ohnuma, Y.; Yamauchi, M.; Tani, H.; Nakamura, A. *Bull. Chem. Soc. Jpn.* 1979, 52, 2036.

Table I. Crystal and Diffraction Data for Compounds 1 and 2a

	1	2a
space group	P2 ₁ /c (No. 14)	P2 ₁ /c (No. 14)
a, Å	7.928 (2)	8.927 (2)
b, Å	18.041 (7)	15.008 (6)
c, Å	15.592 (4)	16.694 (4)
α, deg	90	90
β, deg	92.81 (2)	104.33 (2)
γ, deg	90	90
V, Å ³	2227.6	2166.9
Z	4	4
scan type	ω	θ-2θ
scan rate, deg/min	variable, 3-29	2
2θ min, deg	3	0
2θ max, deg	70	60
no. of refltns measd	7188	5194
no. of refltns with I > 3σ(I)	3443	3144
abs correctn	none	none
final R _F	0.038	0.058
final R _{wF}	0.047	0.088
largest peak in final diff Fourier map, e/Å ³	0.53	0.55

NMR (22 °C, benzene-d₆): δ 3.55-3.1 (complex multiplet, 3, pentadienyl syn H's), 2.0 (s, 6, pentadienyl methyl H's), 1.5-0.8 (complex multiplet, 32, pentadienyl anti H's and triethylphosphine H's). ¹³C{¹H} NMR (22 °C, benzene-d₆): δ 98.7 (C2, C4), 85.1 (C3), 47.6 (C1, C5), 26.7 (pentadienyl methyl C's), 22.0 (triethylphosphine methylene C's), 8.3 (triethylphosphine methyl C's). ³¹P{¹H} NMR (22 °C, benzene-d₆, referenced to internal triethylphosphine): δ 69.4, 38.5. (The two ³¹P{¹H} signals began to broaden and move together around 100 °C, but the sample decomposed at 115 °C, before the signals coalesced). IR (22 °C, benzene): 1023 cm⁻¹ (vs, P-C stretch). Anal. Calcd for CoP₂C₁₉H₄₁: C, 58.44; H, 10.61. Found: C, 58.24; H, 10.46.

C. Synthesis of (anti)-η⁵-2,4-Dimethylpentadienyl)Co[P(CH₃)₃]₃, 2a. A solution of potassium 2,4-dimethylpentadienide-tetrahydrofuran⁴ (2.7 g, 0.013 mol) in tetrahydrofuran was added dropwise to a cold (0 °C) solution of ClCo[P(CH₃)₃]₃⁵ (4.8 g, 0.015 mol) in tetrahydrofuran. The resulting red-brown solution was stirred at 0 °C for 24 h, warmed to room temperature, stirred for an additional 12 h, filtered, and evaporated to dryness. The red-brown product 2a was extracted with pentane and crystallized from a saturated pentane-diethyl ether solution (1:3) at -30 °C: yield of crude product 4.5 g (91%); yield of crystalline product 3.0 g (60%). ¹H NMR (22 °C, benzene-d₆): major (anti) isomer 2a, δ 5.09 (br s, 1, vinyl H), 4.59 (br s, 1, vinyl H), 2.88 (q, 1, J_{H_{allyl(vinyl)}-P} = 5 Hz), 2.43 (q, 1, J_{H_{allyl(vinyl)}-P} = 4 Hz), 2.16 (q, 3, J_{H_{allyl(methyl)}-P} = 3 Hz), 1.92, (s, 3, vinyl methyl H's), 1.06 (t, 27, trimethylphosphine methyl H's) (the resonance of H_{allyl(anti)} was obscured); minor (syn) isomer 2b selected peaks, δ 5.53 (br s, 1, vinyl H), 5.17 (br s, 1, vinyl H), 2.06 (s, 3, vinyl methyl H's). ¹³C{¹H} NMR (22 °C, benzene-d₆): major (anti) isomer 2a, δ 151.0 (C4), 101.8 (C5), 78.1 (C2), 56.8 (C3), 38.1 (C1), 27.4, 26.2 (pentadienyl methyl C's), 22.9 (trimethylphosphine methyl C's); minor (syn) isomer 2b, δ 151.9 (C4), 106.5 (C5), 76.5 (C2), 54.6 (C3), 40.8 (C1), 27.9, 24.5 (pentadienyl methyl C's), 22.4 (trimethylphosphine methyl C's). ³¹P{¹H} NMR (-70 °C, toluene-d₈, referenced to internal P(CH₃)₃): δ 60.3 (s) (the limiting ³¹P{¹H} NMR spectrum was not obtained down to -100 °C⁶). IR (22 °C, benzene): 1610 cm⁻¹ (vs, C=C stretch), 935, 968 cm⁻¹ (vs, P-C stretch). Anal. Calcd for CoP₃C₁₆H₃₈: C, 50.25; H, 10.03. Found: C, 50.00; H, 9.77.

D. X-ray Diffraction Studies of 1 and 2a. Crystals of 1 and 2a were grown from saturated solutions of pentane and pentane-diethyl ether (1:3), respectively, at -30 °C. X-ray diffraction data were collected at room temperature on a Nicolet P3 diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structure refinement were done by using a modified Enraf-Nonius structure determination

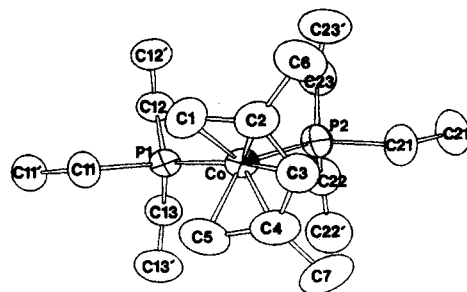
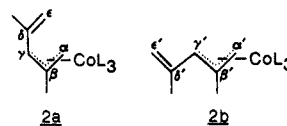


Figure 1. ORTEP drawing for (η⁵-2,4-dimethylpentadienyl)Co[P(C₂H₅)₃]₂, 1. Heavy atoms are represented by thermal vibration spheres drawn to encompass 50% of the electron density. All hydrogen atoms are omitted for clarity.

package⁷ on a VAX 11/780 computer. Crystal data and the details of data collection and structure analysis are summarized in Table I.

The structures of both 1 and 2a were solved by standard Fourier techniques, following the location of the cobalt atoms from Patterson maps. In both structures, the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms in 1 were refined isotropically; those in 2a were not located.

E. Spin Saturation Transfer Experiments Involving 2a and 2b. ¹³C spin saturation transfer experiments⁸ were performed at 70 °C on the University of Illinois—Champaign/Urbana Nicolet NT360 NMR spectrometer. The sample was prepared by dissolving crystalline 2a in benzene-d₆. 2a equilibrated with its isomer 2b to produce a 70:30 mixture of 2a-2b. The labeling scheme for the pentadienyl carbon atoms is shown.



The following pulse sequence was employed: (1) 10-s single-frequency irradiation pulse, (2) 50-ms delay, (3) 3-μs observe pulse, (4) acquisition, (5) 1.0-s delay. The broad-band decoupler was off except during acquisition. The intensities of the signals due to the pentadienyl carbon atoms in 2a (α, β, γ, δ, ε) and 2b (α', β', γ', δ', ε') before irradiation (normal ¹³C{¹H} spectrum), after irradiation at α', and after irradiation at ε' are summarized in Table II. In each case, the intensities are relative to the benzene-d₆ peak at 128.0 ppm, which has a normalized intensity of 1000.

Results and Discussion

A. Synthesis and Structure of (η⁵-2,4-Dimethylpentadienyl)Co[P(C₂H₅)₃]₂, 1. (η⁵-2,4-Dimethylpentadienyl)Co[P(C₂H₅)₃]₂, 1, was synthesized by reacting potassium 2,4-dimethylpentadienide-tetrahydrofuran⁴ (1 equiv) with a tetrahydrofuran solution of CoCl₂ (1 equiv) and triethylphosphine (2 equiv) in the presence of zinc dust (excess). The zinc dust could be replaced by a second equivalent of potassium 2,4-dimethylpentadienide-tetrahydrofuran, which then served as the reducing agent. An ORTEP drawing of 1, based on the X-ray structural analysis, is presented in Figure 1.⁹ Atomic coordinates for the

(7) The programs were modified by B. A. Frenz and Associates, Inc., College Station, TX, 1982.

(8) Faller, J. W. In: "Determination of Organic Structures by Physical Methods"; Nachod, F. C., Zuckerman, J. J., Eds. Academic Press: New York, 1973; Vol. V, Chapter 2.

(9) Because of the rigidity of the η⁵-2,4-dimethylpentadienyl ligand, 1 does not conform to either of the usual coordination geometries for 18-electron Co(I) complexes, i.e., square pyramidal or trigonal bipyramidal. If the 2,4-dimethylpentadienyl group is treated as a single ligand, with the "centroid" (C_p) occupying a single coordination site, the coordination geometry of 1 approximates a trigonal plane. The cobalt atom lies only 0.01 Å out of the plane defined by C_p, P1, and P2. The L-Co-L angles within the trigonal plane are 99.0, 120.8, and 140.2° for P1-Co-P2, P1-Co-C_p, and P2-Co-C_p, respectively. (The "centroid" is taken as the average of the midpoints of vectors C1-C4 and C2-C5.)

(5) Klein, H. F.; Karsch, H. H. *Inorg. Chem.* 1975, 14, 473.

(6) Similar results have been obtained for (η⁵-C₃H₅)Co[P(OCH₃)₃]₃; Muettterties, E. L.; Hirsekorn, F. J. *J. Am. Chem. Soc.* 1974, 96, 7920.

Table II. Peak Intensities^a for Spin Saturation Transfer Experiments Involving 2a and 2b

	α	α'	β	β'	γ	γ'	δ	δ'	ϵ	ϵ'
before irradiatn (normal ¹³ C{ ¹ H} spectrum)	71.46	20.42	22.66	s ^b	65.01	21.64	20.59	s	100.31	36.36
after irradiatn at α'	9.02	0	27.46	s	43.70	11.0	23.06	s	10.17	0
after irradiatn at ϵ'	8.44	0	16.62	s	37.86	11.42	14.22	s	10.30	0

^a Intensities are relative to the benzene-*d*₆ peak at 128.0 ppm, which has a normalized intensity of 1000. ^b s indicates that the peak was clearly present but too small to integrate accurately.

Table III. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in (η^5 -2,4-Dimethylpentadienyl)Co[P(CH₃)₃]₃, 1

atom	x	y	z
Co	0.06450 (4)	0.07607 (2)	0.24337 (2)
P1	0.25411 (9)	-0.00305 (4)	0.21145 (4)
P2	0.22846 (9)	0.16287 (4)	0.29765 (5)
C11	0.1684 (4)	-0.0817 (2)	0.1475 (2)
C12	0.4295 (4)	0.0272 (2)	0.1472 (2)
C21	0.1187 (4)	0.2397 (2)	0.3501 (2)
C22	0.3888 (4)	0.1374 (2)	0.3818 (2)
C23	0.3745 (5)	0.2161 (2)	0.2306 (2)
C13	0.3823 (4)	-0.0523 (2)	0.2961 (2)
C1	-0.0807 (4)	0.0644 (2)	0.1244 (2)
C12'	0.3731 (6)	0.0662 (2)	0.0650 (2)
C11'	0.2855 (5)	-0.1437 (2)	0.1233 (2)
C2	-0.1352 (4)	0.1253 (2)	0.1708 (2)
C21'	0.2219 (5)	0.3016 (2)	0.3926 (3)
C3	-0.1704 (3)	0.1213 (2)	0.2596 (2)
C6	-0.1484 (5)	0.2004 (2)	0.1282 (2)
C13'	0.2822 (6)	-0.0988 (2)	0.3566 (2)
C23'	0.2912 (6)	0.2609 (2)	0.1595 (3)
C22'	0.3155 (6)	0.0999 (2)	0.4568 (2)
C4	-0.1443 (4)	0.0614 (2)	0.3162 (2)
C7	-0.1608 (5)	0.0753 (3)	0.4117 (2)
C5	-0.0989 (4)	-0.0076 (2)	0.2866 (3)

non-hydrogen atoms are listed in Table III; important bond distances and bond angles are listed in Table IV.

The triethylphosphine ligands in 1 are oriented so that P2 eclipses C3 of the 2,4-dimethylpentadienyl ligand, while P1 eclipses the open edge of the 2,4-dimethylpentadienyl ligand.¹⁰ Co, C3, P1, and P2 are coplanar to within 0.020 Å, and the dihedral angle made by this plane with the plane of the pentadienyl ligand (C1, C2, C3, C4, C5) is 88.6°. The Co-P1 bond distance is 2.149 (1) Å, while Co-P2 is 2.180 (1) Å. The distance from the cobalt atom to the five bound pentadienyl carbon atoms range from 2.060 (3) to 2.145 (3) Å. The internal carbon atoms of the pentadienyl ligand (C2, C3, C4) are closer to the cobalt atom than the terminal carbon atoms (C1, C5) are.

Atoms C1, C2, C3, C4, and C5 of the 2,4-dimethylpentadienyl ligand are planar to within 0.039 Å. Methyl carbon atoms C6 and C7 are displaced out of the plane toward the cobalt atom by 0.141 and 0.240 Å, respectively. These displacements are probably a result of the atomic pz orbitals on C2 and C4 bending toward the metal atom to achieve better overlap with the appropriate metal orbitals. The C-C-C angles within the cobalt-bound portion of the 2,4-dimethylpentadienyl ligand are expanded somewhat from the ideal of 120° (122.9 (3), 128.2 (3), and 121.0 (4) for angles C1-C2-C3, C2-C3-C4, and C3-C4-C5, respectively). C-C bond distances within the cobalt-bound portion of the 2,4-dimethylpentadienyl ligand range from 1.381 (5) to 1.428 (5) Å.

B. Synthesis and Structure of (*anti*- η^3 -2,4-Dimethylpentadienyl)Co[P(CH₃)₃]₃, 2a. Synthesis of

(10) This is the preferred conformation for 18-electron (η -polyene)ML₂ complexes: Mingos, D. M. P. In: "Comprehensive Organometallic Chemistry"; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1982; Vol. 3, pp 60-67 and references cited therein.

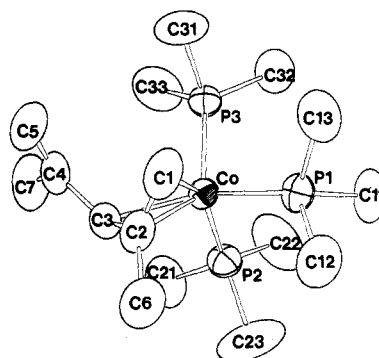


Figure 2. ORTEP drawing for (*anti*- η^3 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₃, 2a. Atoms are represented by thermal vibration spheres drawn to encompass 50% of the electron density.

(*anti*- η^3 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₃, 2a, was effected by reacting ClCo[P(CH₃)₃]₃⁵ with potassium 2,4-dimethylpentadienide-tetrahydrofuran.⁴ An ORTEP drawing of 2a, based on the X-ray structural analysis, is presented in Figure 2. Atomic coordinates for the non-hydrogen atoms are listed in Table V; important bond distances and bond angles are listed in Table VI.

The geometry about the cobalt atom approximates a square pyramid with C1, C3, P1, and P2 occupying the four basal positions and P3 residing in the axial position.¹¹ Salient features of the structure that support the square-pyramidal characterization of the coordination geometry include the following: (a) the Co-P3 bond distance is significantly longer than the Co-P1 and Co-P2 distances (2.197 (1) Å vs. 2.173 (1) and 2.179 (1) Å, respectively); (b) the four P3-Co-(basal atom) angles are all approximately equal (ranging from 100.25 (5) to 105.4 (2)°); (c) the four basal atoms (C1, C3, P1, and P2) are coplanar to within 0.036 Å; the Co atom is displaced by 0.508 Å from their least-squares mean plane toward P3; (d) although the four (basal atom)-Co-(basal atom) angles involving adjacent basal atoms vary substantially (from 69.1 (2) to 97.14 (4)°), this deviation from the ideal is clearly due to constraints imposed on the system by the small bite angle of the η^3 -2,4-dimethylpentadienyl ligand (angle C1-C2-C3 is 115.9 (4)°).^{12,13}

The allylic moiety of the 2,4-dimethylpentadienyl ligand (atoms C1, C2, C6, and C3) has a staggered orientation

(11) The coordination geometries of allylmetal complexes are, in general, best described by treating the allyl group as a bidentate ligand: 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.

(12) The coordination geometries of the closely related compounds (η^3 -C₅H₅)Co(CO)₂[P(C₆H₅)₃] (see a below) and (η^3 -C₅H₁₃)Co[P(OCH₃)₃]₃ (see b below) have also been described as square pyramidal: (a) Rinze, P. V.; Muller, U. *Chem. Ber.* 1979, 112, 1973. (b) Thompson, M. R.; Day, V. W.; Tau, K. D.; Muetterties, E. L. *Inorg. Chem.* 1981, 20, 1237.

(13) Alternatively, the geometry of 2a can be described as tetrahedral, with the three P(CH₃)₃ phosphorus atoms and the "centroid" of the allylic moiety of the 2,4-dimethylpentadienyl ligand, C_a, occupying the four coordination sites. The six L-Co-L angles in this description are 97.1, 100.3, 104.6, 117.0, 120.0, and 114.7° for P1-Co-P2, P1-Co-P3, P2-Co-P3, C_a-Co-P1, C_a-Co-P2, and C_a-Co-P3, respectively. (The "centroid" is taken as the midpoint of vector C1-C3.)

Table IV. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (η^5 -2,4-Dimethylpentadienyl)Co[P(C₂H₅)₃]₂, 1

Bond Distances					
Co-P1	2.149 (1)	P1-C12	1.836 (3)	C23-C23'	1.499 (7)
Co-P2	2.180 (1)	C12-C12'	1.510 (6)	C1-C2	1.396 (5)
Co-C1	2.145 (3)	P1-C13	1.854 (3)	C2-C3	1.428 (5)
Co-C2	2.098 (3)	C13-C13'	1.516 (6)	C3-C4	1.404 (5)
Co-C3	2.060 (3)	P2-C21	1.848 (4)	C4-C5	1.381 (5)
Co-C4	2.070 (3)	C21-C21'	1.518 (6)	C2-C6	1.510 (6)
Co-C5	2.120 (4)	P2-C22	1.840 (4)	C4-C7	1.521 (6)
P1-C11	1.846 (3)	C22-C22'	1.494 (7)		
C11-C11'	1.512 (5)	P2-C23	1.864 (4)		
Bond Angles					
P1-Co-P2	99.01 (3)	C1-C2-C3	122.9 (3)	P1-C12-C12'	113.7 (3)
P1-Co-C1	94.9 (1)	C2-C3-C4	128.2 (3)	Co-P1-C13	121.3 (1)
P1-Co-C3	159.8 (1)	C3-C4-C5	121.0 (4)	P1-C13-C13'	115.0 (3)
P1-Co-C5	92.6 (1)	C1-C2-C6	119.7 (4)	Co-P2-C21	115.2 (1)
P2-Co-C1	133.7 (1)	C3-C2-C6	117.3 (4)	P2-C21-C21'	119.4 (3)
P2-Co-C3	101.1 (1)	C3-C4-C7	118.1 (4)	Co-P2-C22	118.4 (1)
P2-Co-C5	138.6 (2)	C5-C4-C7	120.8 (4)	P2-C22-C22'	112.9 (3)
C1-Co-C3	72.3 (1)	Co-P1-C11	113.1 (1)	Co-P2-C23	121.9 (2)
C3-Co-C5	70.9 (2)	P1-C11-C11'	119.3 (3)	P2-C23-C23'	115.4 (4)
C1-Co-C5	83.9 (2)	Co-P1-C12	119.1 (1)		

Table V. Positional Parameters with Estimated Standard Deviations for Non-Hydrogen Atoms in (*anti*- η^3 -2,4-Dimethylpentadienyl)Co[P(CH₃)₃]₂, 2a

atom	x	y	z
Co	0.20585 (7)	0.13116 (4)	0.25201 (4)
P1	-0.0137 (2)	0.1135 (1)	0.16164 (9)
P2	0.3241 (2)	0.01707 (9)	0.21503 (9)
P3	0.1423 (2)	0.0871 (1)	0.36470 (9)
C1	0.1618 (8)	0.2656 (4)	0.2440 (4)
C2	0.3025 (7)	0.2443 (3)	0.2280 (3)
C6	0.342 (1)	0.2609 (5)	0.1441 (4)
C3	0.4120 (6)	0.2049 (4)	0.2935 (4)
C4	0.4665 (7)	0.2348 (4)	0.3802 (4)
C7	0.605 (1)	0.1847 (5)	0.4305 (5)
C5	0.4109 (9)	0.3054 (4)	0.4131 (4)
C11	-0.1007 (8)	0.0038 (4)	0.1321 (5)
C21	0.5288 (8)	-0.0030 (5)	0.2654 (6)
C31	0.0548 (9)	0.1745 (6)	0.4176 (4)
C12	-0.034 (1)	0.1603 (5)	0.0574 (4)
C22	0.258 (1)	-0.0970 (5)	0.2269 (7)
C32	-0.0016 (9)	-0.0021 (5)	0.3600 (5)
C13	-0.1834 (7)	0.1678 (6)	0.1810 (5)
C23	0.344 (1)	0.0140 (6)	0.1068 (5)
C33	0.2913 (9)	0.0505 (6)	0.4542 (4)

with respect to the P1-P2-P3 face; i.e., the mouth of the allylic moiety faces the axial P(CH₃)₃ ligand and the vinylic moiety (atoms C4, C7, and C5) lies above the basal plane.¹⁴ The cobalt to allylic carbon distances are Co-C1 = 2.053 (4) Å, Co-C2 = 1.990 (4) Å, and Co-C3 = 2.112 (4) Å.

The η^3 -2,4-dimethylpentadienyl ligand is U-shaped; i.e., C1 is syn to C4 and C2 is syn to C5. However, it is *not* planar; the vinylic moiety (atoms C4, C7, and C5) is bent substantially out of the plane of the allylic moiety (atoms C1, C2, C6, and C3) *away from* the cobalt atom. The plane defined by atoms C1, C2, and C3 makes an angle of 37.0° with the C3-C4 vector and intersects the plane defined by atoms C2, C3, and C4 in a dihedral angle of 50.9°. Although the 2,4-dimethylpentadienyl ligand could distort from the U-shaped configuration by rotation about the C3-C4 single bond, it does not. In fact, atoms C2, C3, C4,

C7, and C5 are coplanar to within 0.060 Å.

The angles within the 2,4-dimethylpentadienyl ligand are distorted somewhat from the ideal 120°. Angle C1-C2-C3 is contracted to 115.9 (4)°, while angles C2-C3-C4 and C3-C4-C5 are expanded to 129.2 (4) and 125.0 (5)°, respectively. The C-C bond distances within the allylic moiety of the 2,4-dimethylpentadienyl ligand are 1.385 (7) Å for C1-C2 and 1.404 (6) Å for C2-C3. Bond C3-C4, which is a C-C single bond, has a length of 1.477 (6) Å, while bond C4-C5, a C-C double bond, has a length of 1.344 (7) Å.

C. Solution Dynamics of 2a. In solution, 2a equilibrates with its syn isomer 2b producing a 70:30 mixture of 2a-2b. The two isomers are most clearly seen in the ¹³C{¹H} NMR spectrum, where the five pentadienyl carbon atoms in 2a (α , β , γ , δ , ϵ) and the five pentadienyl carbon atoms in 2b (α' , β' , γ' , δ' , ϵ') all give distinct signals. (The labeling scheme for the pentadienyl carbon atoms is shown in the Experimental Section, part E.) The positions, shapes, and relative intensities of the ¹³C{¹H} signals are essentially invariant within the temperature range of -70 to +70 °C.

¹³C spin saturation transfer experiments⁸ conducted at 70 °C suggest a probable mechanism for the interconversion of 2a and 2b. Irradiation of the signal due to α' in isomer 2b produced a significant loss of intensity in the signals due to ϵ' (isomer 2b), α (isomer 2a), and ϵ (isomer 2a). Similarly, irradiation of the signal due to ϵ' in isomer 2b resulted in significant loss of intensity in the signals due to α' , α , and ϵ . In these irradiations, the signals due to β' , γ' , δ' , β , γ , and δ were essentially unaffected.¹⁵

The spin saturation transfer experiments show clearly that the four terminal carbon atoms of the 2,4-dimethylpentadienyl ligands (α , ϵ , α' , ϵ') are interconverting in solution. The most straightforward mechanistic explanation for these results invokes a C3-bound (η^1 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₂ intermediate in which rotations about single bonds C2-C3 and C3-C4 are unhindered. The (η^1 -2,4-dimethylpentadienyl)Co[P(CH₃)₃]₂ intermediate can revert back to the η^3 -form along any of four equivalent pathways, resulting in interconversion of α' , ϵ' , α , and ϵ

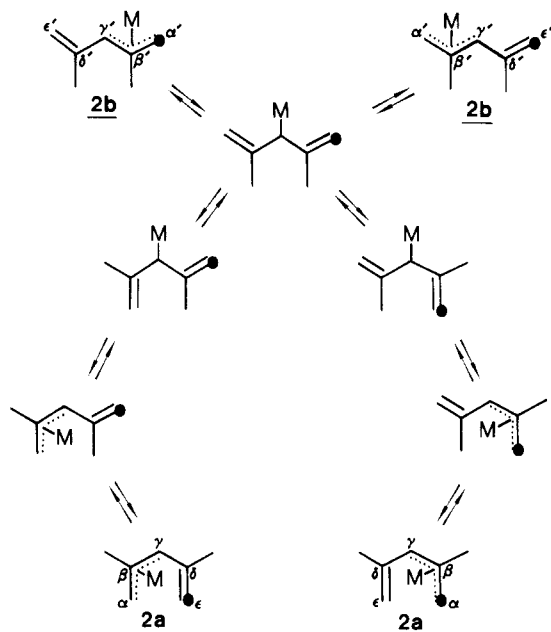
(14) A similar orientation has been observed for the η^3 -allyl ligand in (η^3 -C₃H₅)Co(CO)₂[P(C₂H₅)₃] (see ref 12a) and for the η^3 -cyclooctenyl ligand in (η^3 -C₈H₁₃)Co[P(OCH₃)₃]₃ (see ref 12b). Extended Hückel molecular orbital calculations have shown it to be the most stable orientation for 18-electron (η^3 -allyl)ML₃ systems in general: Albright, T. A.; Hoffmann, P.; Hoffmann, R. *J. Am. Chem. Soc.* 1977, 99, 7546. Harlow, R. L.; McKinney, R. J.; Iltel, S. D. *Ibid.* 1979, 101, 7496.

(15) A small loss in intensity can be attributed to loss of nuclear Overhauser enhancement; the broad-band decoupler was off except during acquisition for the spin saturation experiments, while it was on continuously for the normal spectra.

Table VI. Selected Bond Distances (Å) and Bond Angles (deg) with Estimated Standard Deviations for (*anti*- η^3 -2,4-Dimethylpentadienyl)Co[P(CH₃)₃]₃, 2a

Bond Distances					
Co-P1	2.173 (1)	P1-C12	1.843 (5)	P3-C33	1.822 (5)
Co-P2	2.179 (1)	P1-C13	1.819 (5)	C1-C2	1.385 (7)
Co-P3	2.197 (1)	P2-C21	1.838 (5)	C2-C6	1.545 (7)
Co-C1	2.053 (4)	P2-C22	1.839 (6)	C2-C3	1.404 (6)
Co-C2	1.990 (4)	P2-C23	1.858 (6)	C3-C4	1.477 (6)
Co-C3	2.112 (4)	P3-C31	1.858 (5)	C4-C7	1.510 (7)
P1-C11	1.835 (5)	P3-C32	1.843 (5)	C4-C5	1.344 (7)
Bond Angles					
P1-Co-P2	97.14 (4)	P2-Co-C3	93.5 (1)	C1-C2-C6	123.9 (5)
P1-Co-P3	100.25 (5)	P3-Co-C1	105.4 (2)	C1-C2-C3	115.9 (4)
P1-Co-C1	87.1 (1)	P3-Co-C2	130.2 (1)	C6-C2-C3	120.3 (5)
P1-Co-C2	109.0 (1)	P3-Co-C3	105.4 (1)	C2-C3-C4	129.2 (4)
P1-Co-C3	148.7 (1)	C1-Co-C2	40.0 (2)	C3-C4-C7	114.8 (5)
P2-Co-P3	104.60 (5)	C1-Co-C3	69.1 (2)	C3-C4-C5	125.0 (5)
P2-Co-C1	148.4 (2)	C2-Co-C3	39.9 (2)	C7-C4-C5	119.9 (5)
P2-Co-C2	110.4 (2)				

Scheme I



(and, of course, 2b and 2a) as shown in Scheme I.^{16,17}

Conclusion

The X-ray crystal structures of 1 and 2a and the solution dynamics of 2a (and its isomer 2b) reported herein lend further support to the assertion that acyclic pentadienyl ligands can interact with metal centers through a variety

of energetically accessible bonding modes— η^5 , *anti* η^3 , *syn* η^3 , and η^1 . We anticipate that this versatility will result in interesting and novel reaction chemistry for pentadienylmetal complexes.³ There is also great *potential* for using pentadienylmetal complexes in catalysis, because by shuttling between the various bonding modes, coordination sites can be opened up to accommodate reagents and re-occupied after expulsion of products. We are investigating the reaction chemistry of the pentadienylcobalt phosphine complexes described herein¹⁸ and related systems.

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Registry No. 1, 90991-09-6; 2a, 90991-10-9; 2b, 91050-45-2; CoCl₂, 7646-79-9; ClCo[P(CH₃)₃]₃, 55516-89-7; potassium 2,4-dimethylpentadienide, 74205-98-4.

Supplementary Material Available: Tables of final atomic coordinates, thermal parameters, bond lengths, bond angles, and observed and calculated structure factor amplitudes for both 1 and 2a and, in addition, several significant least-squares planes, including atomic deviations and subtended dihedral angles (48 pages). Ordering information is given on any current masthead page.

(16) $\eta^3 = \eta^1$ isomerizations are common for M-allyl complexes: Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980; pp 133-137 and references cited therein.

(17) An alternative mechanism for isomerizing 2a to 2b, proposed by Professor G. S. Girolami (University of Illinois—Champaign/Urbana), involves sliding the Co[P(CH₃)₃]₃ fragment in a concerted fashion from one end of the 2,4-dimethylpentadienyl ligand (C1, C2, C3) to the other (C3, C4, C5). In this case, the cobalt atom would remain π bonded to the 2,4-dimethylpentadienyl ligand throughout. A similar sliding mechanism has been proposed for isomerizations of (η^3 -polyene)Fe(CO)₂ complexes: Whitlock, H. W., Jr.; Chuah, Y. N. *J. Am. Chem. Soc.* 1965, 87, 3605.

(18) For example, protonation of 1 produces a cationic complex in which the added hydrogen atom appears to be bridging between the cobalt atom and a carbon atom of the 2,4-dimethylpentadienyl ligand. The structure of this cationic complex will be reported in a future communication.