Synthesis, Structure, and Absolute Configuration of Chiral, Pseudooctahedral Perfluoroalkyl-Substituted Dimethylphosphonate Complexes

Chet R. Jablonski,* Huaizhu Ma,[1] and Rosemary C. Hynes[2]

Department of Chemistry, Memorial University, St. John's, Newfoundland, Canada A1B 3X7

Received February 21, 1992

The substitution-labile complexes η^5-CpCo(X)($PPh_2N(R)C^*H(Me)Ph$)(I), **6(a,b)**(α,β), react with trimethyl phosphite to afford η^5-CpCo(X)($PPh_2N(R)C^*H(Me)Ph$)($P(O)(OMe)_2$), **7(a,b)**α, and η^5-CpCo(X)($P(OMe)_3$)(I), **8a,b** (**a**, X = CF_3; **b**, X = n-C_3F_7; α, R = H; β, R = Me). Arbuzov dealkylation to give **7** occurs only for R = H and requires intramolecular P═O⋯H—N hydrogen bonding, which develops early in the transition state to "anchor" the aminophosphine ligand. The chiral, Co-epimeric Arbuzov products were separated and characterized. The absolute configuration of $(+)_{436}$-**7b**α was determined crystallographically. $(+)_{436}$-**7b**α crystallizes in the monoclinic system $P2_1$ with a = 11.0941 (20) Å, b = 16.9200 (22) Å, c = 16.927 (3) Å, β = 91.241 (15)°, V = 3176.6 (9) Å^3, Z = 4, and R_f = 8.4% (R_w = 5.1%) for 1638 reflections with $I > 2.5\sigma I$ and was found to contain two independent molecules in the asymmetric unit. Absolute configurations of $(-)_{436}$-**7b**α, $(-)_{436}$-**7a**α, and $(+)_{436}$-**7a**α were assigned on the basis of chiroptical evidence. P═O⋯H—N hydrogen bonding establishes a pseudoboat conformation with pseudoaxial η^5-Cp and pseudoequatorial n-C_3F_7 in the solid state. Nuclear Overhauser difference (NOED) spectra show that the solid-state conformation persists in solution.

Introduction

Recently we reported[3] evidence demonstrating that a chiral cobalt atom in an asymmetric pseudooctahedral[4,5] environment can function as an effective stereogenic center for the formation of P-chiral phosphonate (:P(O)R(OMe)$^{1-}$) complexes with good optical yields (de ≥ 80%, cf. (Scheme I). Thus, substitution of iodide in the prochiral complex 1 with 1 equiv of $PR(OMe)_2$ gives initially[6-12] the chiral phosphonite complex (R,S_{Co})-2, which subsequently dealkylates via an Arbuzov-like rearrangement[6,8,9,12-18] to afford the phosphonate 3 as a diastereomeric mixture R,S_{Co}; R,S_P. Phosphonato–Co(III) complexes have also been prepared by direct oxidative addition of dialkyl phosphonates ($HP(O)(OR)_2$) to Co(I) substrates[19] and by halide displacement with the corresponding sodium salts.[20] Although the Co– and P–chiral phosphonate products are sufficiently configurationally stable in solution to allow reliable determinations of optical yields, slow epimerization at the cobalt center does occur. We have not examined the Co epimerization of 3 in detail. However, there is ample literature precedent establishing both a dominant dissociative activation mode for loss of stereochemistry at the metal in piano stool complexes[21,22] and the lability of cobalt–halide bonds.[10-12,23,24] It was of interest then, in the context of our studies of optical induction from chiral transition-metal atoms, to prepare derivatives in which this mode of metal epimerization was blocked.[13] This report describes the preparation, characterization, crystal structure, and conformational analysis of the analogous phosphonate derivatives 7 in which iodide is replaced by a substitution-inert perfluoroalkyl group.[13,25]

Results and Discussion

Preparation and Characterization of the Phosphonato Compounds 7a,b. Preferential substitution of labile CO in η^5-CpCo(X)(CO)(I) (X = perfluoroalkyl) by P-donor ligands[13,25,26] occurs even in the absence of halide acceptors[27] and represents a more general synthetic route to the required substrates **6(a,b)**(α,β) than oxidative addition to phosphine-substituted η^5-CpCo(CO)(P-donor) Co(I) complexes.[28] The substitution procedure (cf. Scheme II) reported by Brunner et al.[26] gave good yields of the known complexes **6a**β, **6b**α, and **6b**β as well as the new complex **6a**α. Resolution of the resulting ca. 1:1 mixture of diastereomeric products in the case of **6(a,b)**α was conveniently achieved by fractional crystallization

---

(1) On leave from the Institute of Organic Chemistry Anhui, Normal University, WUHU, Anhui, PRC.

(2) Present address: Chemistry Division, NRC, Ottawa, Canada K1A OR6.

(3) Brunner, H.; Jablonski, C. R.; Jones, P. G. *Organometallics* 1988, 7, 1283–1292.

(4) Reisner, G. M.; Bernal, I.; Brunner, H.; Muschiol, M. *Inorg. Chem.* 1978, *17*, 783–789.

(5) Seeman, J. I.; Davies, S. G. *J. Am. Chem. Soc.* 1985, *107*, 6522–6531.

(6) Haines, R. J.; Du Preez, A. L.; Marais, I. L. *J. Organomet. Chem.* 1971, *28*, 405–413.

(7) Clemens, V.; Neukomm, H.; Werner, H. *Helv. Chim. Acta* 1974, *57*, 2000–2010.

(8) Landon, S. J.; Brill, T. B. *J. Am. Chem. Soc.* 1982, *104*, 6571–6575.

(9) Brill, T. B.; Landon, S. J. *Inorg. Chem.* 1984, *23*, 1266–1271.

(10) Brill, T. B.; Landon, S. J. *Inorg. Chem.* 1984, *23*, 4177–4181.

(11) Brill, T. B.; Landon, S. J. *Inorg. Chem.* 1985, *24*, 2863–2864.

(12) Schleman, E. V.; Brill, T. B. *J. Organomet. Chem.* 1987, *323*, 103–109.

(13) Brunner, H.; Riepl, G.; Benn, R.; Rufinska, A. *J. Organomet. Chem.* 1983, *253*, 93–115.

(14) King, R. B.; Reimann, R. H. *Inorg. Chem.* 1976, *15*, 179–183.

(15) Werner, H.; Neukomm, H.; Klaui, W. *Helv. Chim. Acta* 1977, *60*, 326–333.

(16) Toscano, P. J.; Marzilli, L. G. *Inorg. Chem.* 1979, *2*, 421–424.

(17) Werner, H.; Juthani, B. *J. Organomet. Chem.* 1981, *209*, 211–218.

(18) Brill, T. B.; Landon, S. J. *Chem. Rev.* 1984, *84*, 577–585.

(19) Mitchell, T. R. B. *J. Organomet. Chem.* 1984, *270*, 245–250.

(20) Pidcock, A.; Waterhouse, C. R. *J. Chem. Soc. A* 1970, 2080–2086, 2087–2093.

(21) Brunner, H.; Vogt, H. *J. Organomet. Chem.* 1981, *210*, 223–236.

(22) Brunner, H. In *Advances in Organometallic Chemistry*; Stone, F. G. A., West, R., Eds.; Academic Press: New York, 1980; pp 151–206.

(23) Towle, D. K.; Landon, S. J.; Brill, T. B.; Tulip, T. H. *Organometallics* 1982, *1*, 295–301.

(24) Bernal, I.; Reisner, G. M.; Brunner, H.; Riepl, G. *J. Organomet. Chem.* 1985, *284*, 115–128.

(25) Brunner, H.; Rambold, W. *J. Organomet. Chem.* 1974, *64*, 373–383.

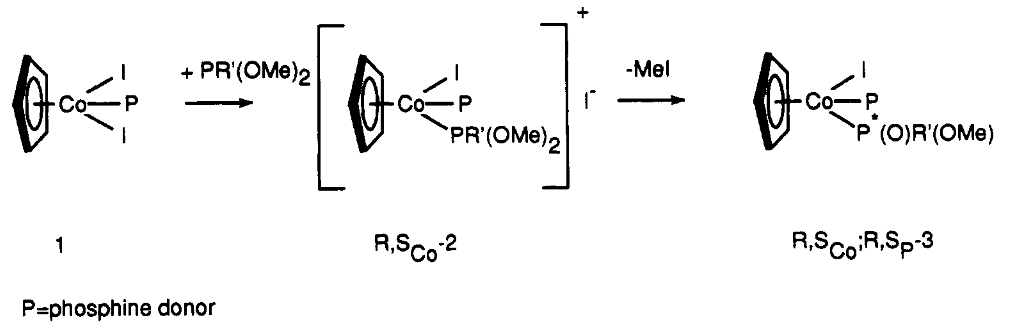
(26) Brunner, H.; Doppelberger, J.; Dreischl, P.; Mollenberg, T. *J. Organomet. Chem.* 1977, *139*, 223–233.

(27) Treichel, P. M.; Werber, G. *Inorg. Chem.* 1965, *4*, 1098–1102.

(28) King, R. B. *Inorg. Chem.* 1966, *5*, 82–87.

0276-7333/92/2311-2796$03.00/0

Scheme I



Scheme II

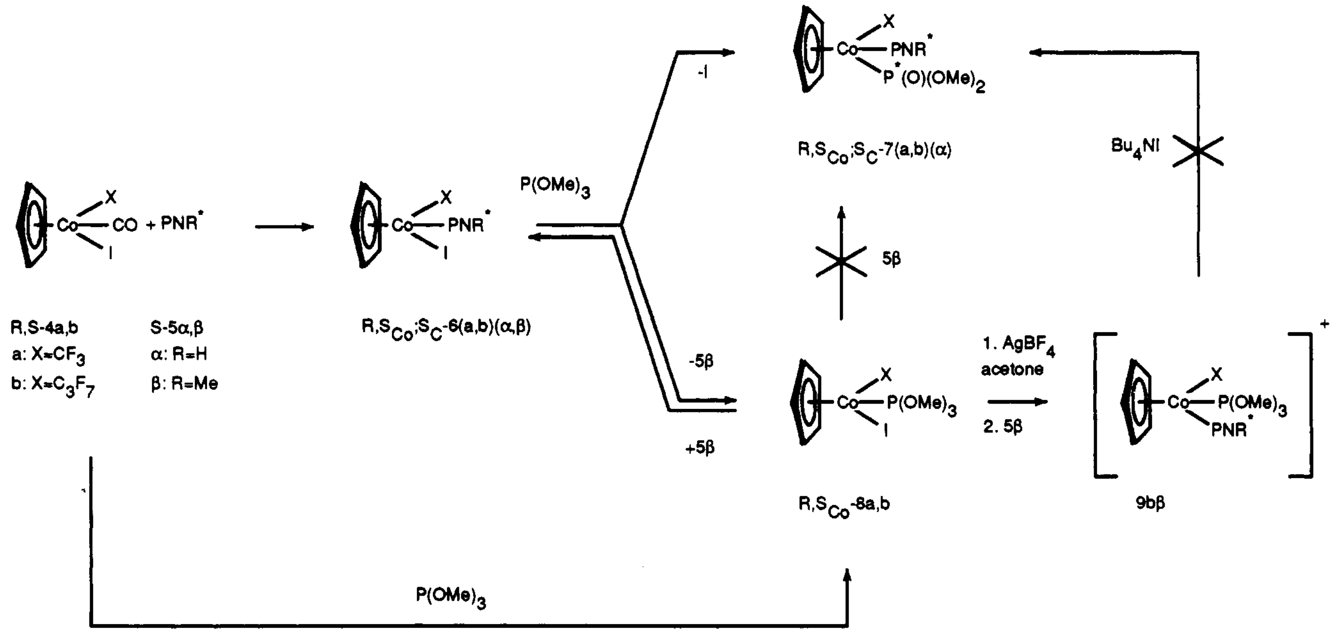


Table I. Analytical and Physical Data

compd	formula	% C found (calcd)	% H found (calcd)	% N found (calcd)	mp	color
6aα	$C_{26}H_{25}CoF_3NP$	49.474 (49.94)	4.03 (4.03)	2.24 (2.24)		purple
$(-)_{436}$-**7a**α	$C_{28}H_{31}CoF_3NO_3P_2$				183–184	orange
$(+)_{436}$-**7a**α	$C_{28}H_{31}CoF_3NO_3P_2$	55.00 (55.37)	5.08 (5.14)	2.22 (2.31)	188–189	orange
$(-)_{436}$-**7b**α	$C_{30}H_{31}CoF_7NO_3P_2$	51.38 (50.93)	4.47 (4.42)	1.91 (1.98)	133–134	orange
$(+)_{436}$-**7b**α	$C_{30}H_{31}CoF_7NO_3P_2$				157–158	orange
8a	$C_9H_{14}CoF_3IO_3P$	23.94 (24.35)	2.86 (3.18)		138–139	purple-black
8b	$C_{10}H_{14}CoF_7IO_3P$	22.58 (22.58)	2.65 (2.65)		186–187 (dec)	purple-black

from methylene chloride/hexane. The diastereomers of **6b**α show distinctive ^1H NMR spectra[26] in $CDCl_3$ (less soluble diastereomer, Cp, 4.98 ppm, s; CMe, 0.92 ppm, d, J = 6.8 Hz; more soluble diastereomer, Cp, 4.93 ppm, s; CMe, 1.34 ppm, d, J = 6.8 Hz.). The chiral cobalt center in (R,S_{Co})-**6(a,b)**(α,β) is stereolabile[26] at temperatures required for further reaction according to Scheme II; hence, diastereomeric mixtures were used for all subsequent reactions.

The deep-purple perfluoroalkyl complexes **6(a,b)**(α,β) exhibit two parallel reaction channels on treatment with trimethyl phosphite. The *sec*-aminophosphine[29] complexes **6(a,b)**α react predominantly via iodide displacement/Arbuzov dealkylation to give orange phosphonato products **7(a,b)**α (cf. discussion below), while the *tert*-aminophosphine complexes **6(a,b)**β prefer to substitute a more labile aminophosphine ligand. The purple perfluoroalkyl phosphite complexes **8a,b** isolated in the latter case were characterized spectroscopically (cf. Tables II and III) and by direct preparation from the parent CO complexes **4a,b** (cf. Scheme II).

Attempts to prepare dimethylphosphonato complexes containing the *tert*-aminophosphine via a two-step sequence involving iodide substitution followed by dealkylation failed. NMR experiments showed that direct reaction of **8a** with **5**β in benzene at 60 °C or acetone at 25 °C results in slow, incomplete phosphite substitution to give **6(a,b)**β. Directed halide substitutions also failed. Treatment of **8b** with $AgBF_4$ in acetone gave a yellow precipitate of AgI and the expected labile solvent complex, which was characterized by its ^1H NMR spectrum (Cp, 5.63 ppm, s; $P(OMe)_3$, 3.93 ppm; d, J = 10.7 Hz). In situ treatment of the acetone complex with aminophosphine **5**β in an NMR tube afforded **9b**β, presumably the same intermediate required[18] in the Arbuzov sequence leading to **7b**β. The structure of **9b**β is supported by its ^1H NMR

---

[29] By analogy with the accepted nomenclature for amines, compound **5**α, which has one remaining unsubstituted N–H, is referred to as primary, while **5**β, which has no remaining N–H groups, is tertiary.

Table II. ^{1}H and ^{19}F NMR Data[a]

compd	Ph	NR	Cp	OMe	C*H	C*Me	CF_3/n-C_3F_7
6aα	8.23 (m) 7.9–6.8 (m)	3.19 (dd, 15.2, 10.5),[b] 3.30 (dd, 17.3, 10.3)	4.93 4.98		3.83 (m) 3.91 (m)	1.34 (d, 6.8), 0.92 (d, 6.8)	6.74 (s) 6.29 (s)
$(-)_{436}$-**7aα**	7.72 (m), 7.51 (m), 7.13 (m), 7.02 (m), 6.90 (m)	6.48 (dd, 17.5, 10.7)	4.87 (s)	3.82 (d, 10.3), 3.80 (d, 11.9)	3.73 (m)	1.41 (d, 6.8)	7.13 (s)
$(+)_{436}$-**7aα**	7.81 (m), 7.49 (m), 7.31 (m), 7.18 (m)	6.30 (dd, 15.8, 9.9)	4.92 (s)	3.82 (d, 10.5), 3.77 (d, 11.1)	3.8 (m)	0.94 (d, 6.7)	7.88 (s)
$(-)_{436}$-**7bα**	7.67 (m), 7.53 (m), 7.13 (m), 6.94 (m), 6.81 (m)	6.42 (dd, 18.2, 10.2)	4.94 (s)	3.84 (d, 10.3), 3.77 (d, 11.2)	3.59 (m, 9.1, 10.2, 7.0)[c]	1.43 (d, 6.8)	α: −70.1, −66.3 (m, 279)[d] β: −115.7, −115.6 (m, 279)[d] γ: −79.0 (t, 12.1)
$(+)_{436}$-**7bα**	7.95 (m), 7.50 (m), 7.35 (m), 7.12 (m), 6.95 (m), 6.81 (m)	6.22 (dd, 16.9, 9.6)	5.01 (s)	3.83 (d, 10.5), 3.77 (d, 11.0)	3.67 (m)	1.03 (d, 6.7)	α: −67.3, −68.3 (m, 273)[d] β: −115.8, −115.1 (m, 277)[d] γ: −79.0 (t, 12.8)
8a			5.29 (s)	3.82 (d, 10.6)			8.93 (s)
8b			5.28 (d, 0.4)	3.82 (d, 10.6)			α: −56.6, −68.2 (m, 257)[d] β: −113.0, −115.0 (m, 282)[d] γ: −79.33 (s)

[a] ^{1}H (300.1 MHz) NMR chemical shifts in ppm relative to internal TMS; ^{19}F (282.37 MHz) NMR chemical shifts relative to internal $CFCl_3$; m = multiplet; s = singlet; d = doublet; u = unresolved; J values given in Hz; solvent = $CDCl_3$. [b] ($^2J_{HP}$, $^3J_{HH}$). [c] ($^3J_{PH}$, $^3J_{NHH}$, $^3J_{HH}$). [d] AB multiplet, $^4J_{FF}$ and $^3J_{FF}$ unresolved.

Table III. ^{13}C NMR Data[a]

compd	C–Ph	P–Ph	Cp	OMe	C*	C*Me*
6aα	i: 145.50, 144.73 *o*/*m*: 128.31, 127.88 *o*/*m*: 125.57, 125.27 *p*: 126.57, 125.87	i: 135.08 (d, 49.4), 133.84 (d, 51.3) *o*/*m*: 133.31 (d, 9.7), 133.18 (d, 9.4), 131.95 (d, 10.4), 131.71 (d, 9.7) *o*/*m*: 128.53 (d, nm), 127.95 (d, nm), 127.70 (d, nm), nm *p*: 131.42, 130.86, 130.76, 130.56	81.39		54.30 (d, 10.1) 54.17 (d, 10.1)	27.54 (d, 7.4) 25.74 (d, 7.6)
$(-)_{436}$-**7aα**	i: 146.27 *o*/*m*: 127.32 *o*/*m*: 125.67 *p*: 125.38	i: 135.75 (d, 54.0), 134.58 (d, 56.9) *o*/*m*: 128.10 (d, 10.3), 127.38 (d, 9) *o*/*m*: 132.43 (d, 10.9), 131.98 (d, 9.8) *p*: 130.27, 129.97	90.57	54.15 (d, 10.2) 50.09 (d, 9.9)	52.77 (d, 6.8)	27.57 (d, 7.3)
$(+)_{436}$-**7aα**	i: 146.20 *o*/*m*: 128.08 *o*/*m*: 125.76 *p*: 126.08	i: 137.14 (d, 49.5), 134.17 (d, 59.0) *o*/*m*: 132.51 (d, 9.8), 132.38 (d, 9.2) *o*/*m*: 128.15 (d, 11.0), 127.67 (d, 10.5) *p*: 130.55, 130.18	90.60	53.81 (d, 10.7) 50.51 (d, 10.2)	52.50 (d, 6.9)	26.37
$(-)_{436}$-**7bα**	i: 146.78 *o*/*m*: 127.42 *o*/*m*: 125.74 *p*: 125.49	i: 136.20 (d, 60.8), 143.15 (d, 60.0) *o*/*m*: 128.03 (d, 10.5), 127.24 (d, 10) *o*/*m*: 132.30 (d, 10.3), nm *p*: 130.20, 129.88	89.34	53.30 (d, 9.8) 50.20 (d, 11.0	53.06 (d, nm)	27.51 (d, 5.5)
$(+)_{436}$-**7bα**	i: 146.24 *o*/*m*: 128.11 *o*/*m*: 125.90 *p*: 126.18	i: 137.40 (d, 60.8), 134.30 (d, 61) *o*/*m*: 128.0 (d, 10.5), 127.51 (d, 10.7) *o*/*m*: 132.78 (d, 10.1), nm *p*: 130.48, 130.01	89.38	54.03 (d, 10.8) 50.65 (d, 9.4)	52.78 (d, 10.8)	26.63
8a			89.21	55.15 (d, 7.5)		
8b			88.08	55.349 (d, 6.6)		

[a] ^{13}C (75.47 MHz) NMR chemical shifts in ppm relative to $CDCl_3$ = 77.0; d = doublet; nm = not measured; J values in Hz.

Table IV. Preparative Conditions for 6(a,b)(α,β) and 8a,b

compd	solvent	time, h	temp, °C	elution EtOAc:hexane	% yield
6aα	CH_2Cl_2	2.0	20	1:5	95
6aβ	CH_2Cl_2	14.0	20	1:2	95
6bα	CH_2Cl_2	2.0	20	1:15	92
6bβ	CH_2Cl_2	0.25	20	1:2	95
8a	CH_2Cl_2	1.0	20	1:3	80
8b	CH_2Cl_2	1.0	20	2:5	63

spectrum, which shows signals for Cp (5.58 ppm, d, $^2J_{HP}$ = 0.4 Hz), $P(OMe)_3$ (3.92 ppm, d, $^3J_{HP}$ = 10.7 Hz), and coordinated **5β** (PPh 7.5 ppm, m; NMe 2.40 ppm, d, $^3J_{PH}$ = 6.5 Hz; CMe 1.63 ppm, d, ^3J = 6.9 Hz; CH 5.15 ppm, m). Two Co epimers of **9bβ** are expected. However, the ^{1}H NMR spectrum was consistent with the presence of a single diastereomer. Presumably the Co configuration is labile,[26,30] and the equilibrium strongly favors[13] one epimer. Treatment of **9bβ** with iodide (as NaI or $(n\text{-}C_4H_9)_4NI$) did not result in dealkylation since no methyl iodide was detected via ^{1}H NMR. Traces of the simple Co-substitution product **8b** but no coordinated **5β** were observed.

Unlike the *tert*-aminophosphine derivatives, complexes **6(a,b)α** react smoothly with trimethyl phosphite in benzene to afford phosphonato products via an Arbuzov-like rearrangement. The orange phosphonato products **7(a,b)α** form as a ca. 50/50 mixture of diastereomers

---

(30) Bernal, I.; Reisner, G. M.; Brunner, H.; Riepl, G. *Inorg. Chim. Acta* **1985**, *103*, 179–185.

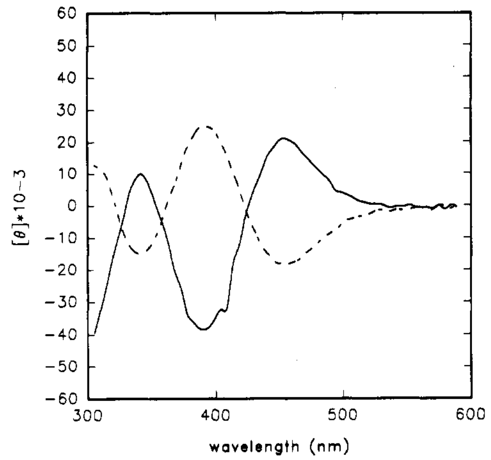


Figure 1. Circular dichroism spectra of $(-)_{436}$-**7bα** (solid line) and $(+)_{436}$-**7bα** (dotted line) in toluene.

differing only in the configuration at the cobalt atom. Separation of the diastereomeric mixture was readily accomplished using radial thick layer chromatography followed by crystallization from methylene chloride/hexane. The Co-epimeric diastereomers are configurationally stable in solution. A sample of diastereomerically pure **7bα** was heated at 60 °C for several weeks in a sealed NMR tube without any measurable isomerization. The higher R_f zone for both **7aα** and **7bα** was determined to be levorotatory ($[\alpha]_{436} = -2192$ and -2090, respectively), while the lower R_f zones were dextrorotatory ($[\alpha]_{436} = 2040$ and 3095, respectively). Their structures are supported by ^{1}H, ^{19}F, and ^{13}C NMR data. Distinctive pairs of diastereotopic methoxy doublets are observed in the ^{1}H and ^{13}C NMR spectra for each Co epimer (cf. Tables II and III). The n-C_3F_7 derivatives also show well-resolved ^{19}F AB patterns[31] for the diastereotopic α-CF_2 and β-CF_2 groups[32] (cf. Table II). However, the expected $^4J_{FF}$ and much smaller $^3J_{FF}$ couplings of the seven-spin ABMNX$_3$ system were not resolved. Characteristically, the ^{1}H NMR chemical shift parameters correlate with the chromatographic R_f value as well as the chiroptical properties (cf. discussion below) for each pair of diastereomers examined in this study. As found previously for other pairs of related Co-epimeric phosphonato complexes[3] the ^{1}H NMR chemical shift of C*–Me in the higher R_f $(-)_{436}$-**7a,bα** is in each case *less* shielded than its lower R_f $(+)_{436}$ diastereomer. The expected[3] P=O stretch at ca. 1150 cm^{-1} was obscured by strong CF absorptions.

Absolute Configurations of $(\pm)_{436}$-7(a,b)α. The absolute configurations of $(\pm)_{436}$-**7(a,b)α** were assigned on the basis of circular dichroism (CD) spectra and, in the case of $(+)_{436}$-**7bα**, crystallographic evidence. Figures 1 and 2 show that the CD spectra of the high- and low-R_f diastereomers of **7(a,b)α** are quasi-mirror images as expected for piano stool transition-metal epimers.[3,22,33] A single-crystal X-ray structure of low-R_f $(+)_{436}$-**7bα** allows unambiguous assignment[34] of its absolute configuration at the chiral cobalt center (cf. Figures 3 and 4) as well as confirmation of the absolute configuration at carbon which was known to be *S*. The absolute configurations for $(+)_{436}$-**7bα** and $(+)_{436}$-**7bα′** were determined using the NRCVAX utility

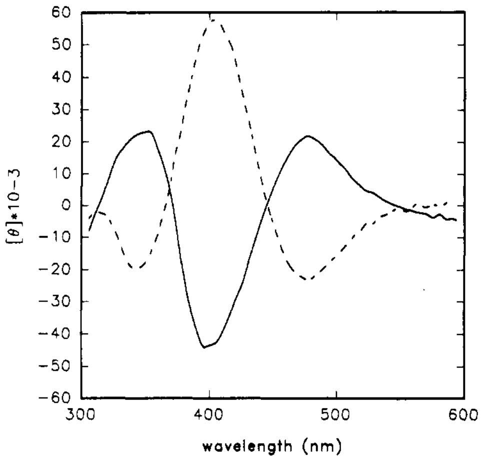


Figure 2. Circular dichroism spectra of $(-)_{436}$-**7aα** (solid line) and $(+)_{436}$-**7aα** (dotted line) in toluene.

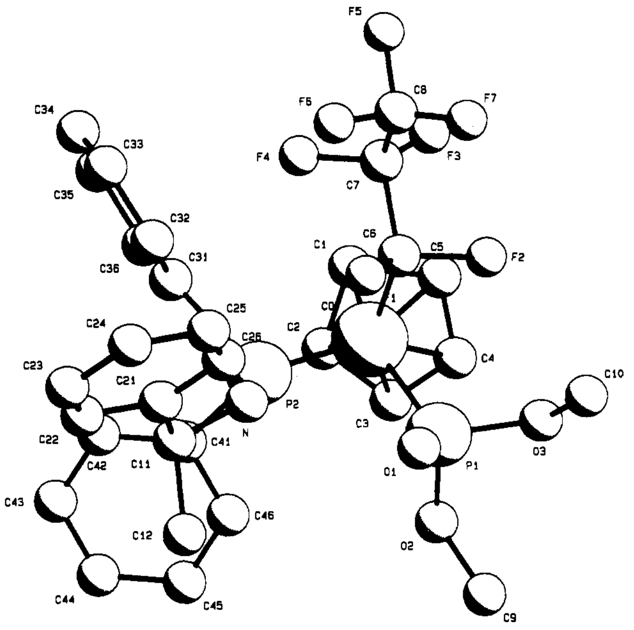


Figure 3. Molecular geometry and absolute configuration of $(+)_{436}$-**7bα**.

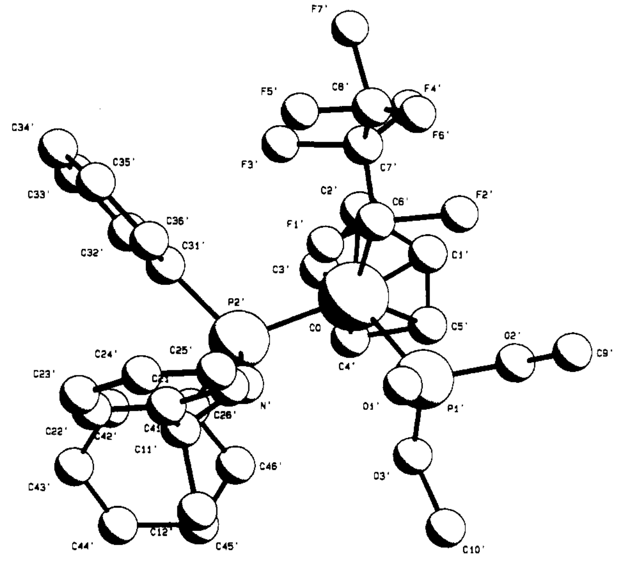


Figure 4. Molecular geometry and absolute configuration of $(+)_{436}$-**7bα′**.

BIVOET[35] in which a solved structure is used to identify the Friedel pairs most affected by anomolous dispersion and

---

(31) Brunner, H.; Rambold, W. *J. Organomet. Chem.* **1973**, *60*, 351–361.

(32) Treichel, P. M.; Stone, F. G. A. S. *Adv. Organomet. Chem.* **1964**, *1*, 143–220.

(33) Jablonski, C. R.; Burrow, T.; Jones, P. G. *J. Organomet. Chem.* **1989**, *370*, 173–185.

(34) Rogers, D. *Acta. Crystallogr., Sect A: Found Crystallogr.* **1981**, *37*, 734–741.

Table V. Nuclear Overhauser Difference Data[a]

	observed NOE,[a] %						
compd	OPh[b,c]	OPh[b,d]	NH	Cp	OMe[c]	OMe[d]	CMe
$(-)_{436}$-**7a**α	1.0	1.0	(100)	0	0[e]	0[e]	1.0
$(+)_{436}$-**7a**α	1.1	0.8	(89)	0	0[e]	0[e]	1.0
$(-)_{436}$-**7b**α	0.7	1.0	(72)	0	0	0	0.7
$(+)_{436}$-**7b**α	1.5	1.2	(73)	0	0	0	0.9
$(-)_{436}$-**7a**α	3.7	3.6	0	(91)	0.1[f]	0.1[f]	0
$(+)_{436}$-**7a**α	3.3	4.5	0	(94)	0.3[f]	0.3[f]	0
$(-)_{436}$-**7b**α	6.4	5.8	0	(92)	1.3	1.1	0.5
$(+)_{436}$-**7b**α	5.5	6.9	0	(88)	0.4	0.6	0
$(-)_{436}$-**7a**α	3.2	3.9	1.9	0.4	(74)[f,g]	(74)[f,g]	1.3
$(+)_{436}$-**7a**α	4.8	2.6	2.0	0.8	(77)[f,g]	(77)[f,g]	1.7
$(-)_{436}$-**7b**α	1.3	0.7	0.6	1.5	(99)[g]		
$(+)_{436}$-**7b**α	0.7	0.3	0.7	0.5	(74)		
$(-)_{436}$-**7b**α	1.3	1.2	0.5	1.4		(79)[g]	
$(+)_{436}$-**7b**α	1.8	0.6	1.7	0.4		(69)	
$(-)_{436}$-**7a**α	3.9	0.9	5.6	0	0[e]	0[e]	(88)
$(+)_{436}$-**7a**α	2.4	1.2	5.4	0	0[e]	0[e]	(88)
$(-)_{436}$-**7b**α	6.2	0	2.4	0.9	1.0	1.0	(73)
$(+)_{436}$-**7b**α	2.5	0	5.0	0.2	0.1	1.4	(75)

[a] % reduction of irradiated peak in parentheses; NOE enhancement in % ± 0.5. [b] Assigned to *o*-phenyl protons of PPh_2. [c] Low field. [d] High field. [e] Corrected for overlapping C*H signal. [f] Averaged value. [g] C*H also irradiated.

Table VI. Selected Bond Distances for $(+)_{436}$-7bα

	distance, Å	
	$(+)_{436}$-**7b**α[a]	$(+)_{436}$-**7b**α'[a]
Co–P(1)	2.223 (14)	2.233 (17)
Co–P(2)	2.219 (9)	2.219 (10)
Co–C(1)	2.08 (4)	2.03 (4)
Co–C(2)	2.10 (4)	2.15 (4)
Co–C(3)	2.09 (4)	2.20 (4)
Co–C(4)	2.07 (9)	2.16 (4)
Co–C(5)	2.05 (4)	2.12 (5)
Co–C(6)	2.03 (4)	2.04 (6)
P(1)–O(1)	1.48 (3)	1.45 (3)
P(1)–O(2)	1.63 (2)	1.63 (3)
P(1)–O(3)	1.64 (2)	1.58 (3)
P(2)–N	1.64 (3)	1.67 (3)
P(2)–C(31)	1.853 (20)	1.825 (22)
P(2)–C(41)	1.801 (21)	1.828 (20)
F(1)–C(6)	1.40 (5)	1.47 (6)
F(2)–C(6)	1.39 (4)	1.52 (7)
F(3)–C(7)	1.32 (5)	1.52 (7)
F(4)–C(7)	1.38 (6)	1.26 (7)
F(5)–C(8)	1.39 (7)	1.35 (10)
F(6)–C(8)	1.27 (7)	1.13 (10)
F(7)–C(8)	1.23 (7)	1.46 (10)
O(2)–C(9)	1.49 (5)	1.43 (5)
O(3)–C(10)	1.43 (6)	1.53 (6)
N–C(11)	1.47 (4)	1.48 (3)
C(1)–C(2)	1.42 (5)	1.39 (7)
C(1)–C(5)	1.46 (5)	1.29 (6)
C(2)–C(3)	1.37 (6)	1.29 (7)
C(3)–C(4)	1.25 (6)	1.35 (6)
C(4)–C(5)	1.34 (6)	1.40 (7)
C(6)–C(7)	1.559 (6)	1.36 (9)
C(7)–C(8)	1.55 (8)	1.57 (11)
C(11)–C(12)	1.55 (4)	1.51 (4)
N–HN	1.080 (24)	1.08 (3)

[a] Parameters reported for both independent molecules in the unit cell.

Table VII. Selected Bond Angles for $(+)_{436}$-7bα

	angles, deg	
	$(+)_{436}$-**7b**α[a]	$(+)_{436}$-**7b**α'[a]
P(1)–Co–P(2)	95.2 (4)	94.6 (5)
P(1)–Co–C(6)	89.4 (13)	86.8 (2)
P(2)–Co–C(6)	94.4 (12)	99.1 (16)
Co–P(1)–O(1)	120.5 (11)	115.0 (14)
Co–P(1)–O(2)	109.8 (14)	108.7 (12)
Co–P(1)–O(3)	111.9 (11)	104.6 (14)
O(1)–P(1)–O(2)	100.0 (16)	113.9 (17)
O(1)–P(1)–O(3)	104.1 (16)	112.1 (17)
O(2)–P(1)–O(3)	98.1 (14)	101.3 (15)
Co–P(2)–N	114.3 (10)	113.5 (11)
N–P(2)–C(31)	108.8 (13)	108.2 (13)
N–P(2)–C(41)	105.9 (13)	103.4 (12)
C(31)–P(2)–C(41)	102.6 (11)	101.3 (11)
P(1)–O(2)–C(9)	119 (3)	124.9 (24)
P(1)–O(3)–C(10)	121 (3)	120 (3)
P(2)–N–C(11)	123.9 (21)	126 (3)

[a] Parameters reported for both independent molecules in the unit cell.

to compare the calculated relative magnitudes of F(+++) and F(−−−) with those measured. The hand of the working model was confirmed. The probability of this assignment being incorrect is was calculated[35] to be 2×10^{-8}.

Consideration of the chiral complex $(+)_{436}$-**7(a,b)**α as a pseudotetrahedral case with η^5-Cp effectively occupying one coordination site and use of the modified Cahn–Ingold–Prelog rules[36–38] with the ligand priority series Cp > $P(O)(OMe)_2$ > (*S*)-(−)-$PPh_2NHCH(Me)Ph$ > X fixes its absolute configuration as S_{Co}; S_C. CD spectra confirm that $(-)_{436}$-**7(a,b)**α is its Co epimer with absolute configuration R_{Co}; S_C. Since the CD spectra of high-R_f $(-)_{436}$-**7a**α and high-R_f $(-)_{436}$-**7b**α are isomorphous, the former can be assigned the absolute configuration R_{Co}; S_C. Similarly, CD data allow assignment of the low-R_f $(+)_{436}$-**7a**α diastereomer as S_{Co}; S_C.

Crystal Structure and Solid-State Conformation. Suitable crystals of $(+)_{436}$-**7b**α were obtained by slow cooling of methylene chloride/hexane solutions. The solid-state structure, determined by X-ray techniques (cf. Experimental Section for details), revealed two crystallographically independent molecules in the asymmetric unit ($Z = 4$). Positional parameters and selected bond lengths and angles are given in Tables VI and VII. Representational drawings, shown in Figure 3 and 4, define piano stool structures with approximate 90° bond angles about a pseudooctahedral cobalt. The coordination sphere consists of an unexceptional η^5-Cp ring which occupies three *facial*

---

(35) Le Page, Y.; Gabe, E. J.; Gainsford, G. J. *J. Appl. Crystallogr.* **1990**, *23*, 406–411.

(36) Cahn, R. S.; Ingold, C.; Prelog, V. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 385–415.

(37) Lecomte, C.; Dusavsoy, Y.; Protas, J.; Tirouflet, J.; Dormand, A. *J. Organomet. Chem.* **1974**, *73*, 67–76. Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598–6599.

(38) Sloan, T. E. *Top. Stereochem.* **1981**, *12*, 1–36.

Table VIII. Summary of Crystallographic Data for $(+)_{436}$-7bα[a]

formula	$C_{30}H_{31}CoNO_3P_2F_7$
M	707.45
crystal habit	orange prism
crystal size, mm	0.3 × 0.1 × 0.03
crystal system	monoclinic
space group	$P2_1$
cell constants	
a, Å	11.0941 (20)
b, Å	16.9200 (22)
c, Å	16.927 (3)
β, deg	91.241 (15)
V, Å^3	3176.6 (9)
Z	4
D_x, g cm^{-3}	1.479
$F(000)$	1447.80
scan type	$\theta/2\theta$
abs correction	none
$2\theta_{max}$, deg	44.8
h,k,l ranges	−11,11,0; 17,0,18
reflns measd	5010
unique reflns	4957
obsd reflns ($I_{net} > 2.5\sigma I_{net}$)	2042
R_f ($I > 2.5\sigma(I)$)	0.084
R_w ($I > 2.5\sigma(I)$)	0.051
GOF	1.97
no. of params	360
largest peak in final diff map, e$^-$ Å^{-3}	0.450
deepest hole in final diff map, e$^-$ Å^{-3}	−0.420

[a] $R_f = \sum(F_o - F_c)/\sum F_o$; $R_w = (\sum(w(F_o - F_w)^2)/\sum(wF_o^2))^{1/2}$; GOF $= (\sum(w(F_o - F_w)^2)/(\text{no. reflns} - \text{no params}))^{1/2}$.

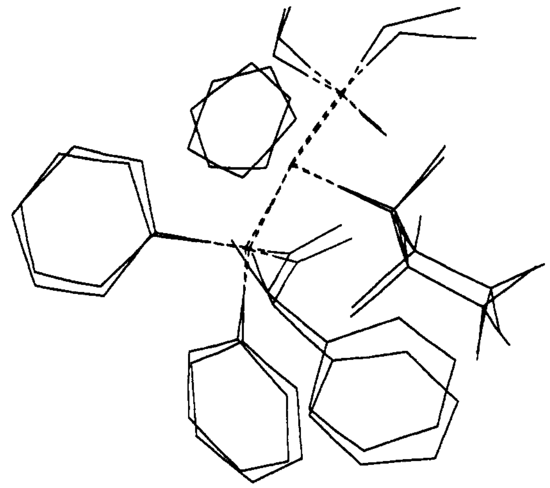


Figure 5. Comparison of conformations for $(+)_{436}$-**7bα** and $(+)_{436}$-**7bα′**.

coordination sites. A P-bound dimethylphosphonato[20] group, an aminophosphine, and a perfluoropropyl group fill the remaining coordination positions. Except for a minor change in orientation of the η^5-Cp ring (cf. Figure 5), the fundamental structure of the two independent molecules is identical. Both the P(N)–Co–P(O) and the P(N)–Co–C bond angles open slightly to ca. 95° in order to accommodate the steric requirement of the aminophosphine ligand. No significant differences in C–P bond lengths were apparent for the aminophosphine and dimethylphosphonate ligands. As found previously,[3,23,39] the geometry of the dimethylphosphonate ligand is distorted from tetrahedral by a closing of the O—P—O angle to 102° and a concomitant opening of the Co—P=O angle to 121°.

Strong intramolecular N—H···O=P hydrogen bonding is evident in the solid-state structure. The N–O bond distance of 2.843 Å for $(+)_{436}$-**7bα** is markedly less than the value of 3.0516 Å typically found for strongly hydrogen-bonded O···H–N systems.[40] The secondary hydrogen-bonding interaction controls the solid-state conformation and results in a distorted six-membered (Co–P–O···H–N–P) boat. As found previously[3,40] for related complexes containing the aminophosphine ligand **5α** and an accessible oxygen-donor site, the η^5-Cp ring assumes a pseudoequatorial position bisecting both the PPh_2 and $P(OMe)_2$ groups. This conformation places the ortho protons of *both* phenyl groups proximal (ca. 2.3 Å to the η^5-Cp ring hydrogens) and, as a further consequence, forces the η^5-Cp ring and N(R)C* into a anti rather than the preferred[41] gauche relationship. The planes of the pseudoequatorial PPh and η^5 groups are also orthogonal, allowing for an attractive β-phenyl effect.[24,42] Since the alternate conformation which places a perfluoroalkyl group pseudoequatorial and η^5-Cp pseudoaxial would also permit the preferred gauche η^5-Cp/N(R)C* arrangement[41] as well as the stabilizing β-phenyl effect, we are forced to conclude that a further destabilizing steric interaction must be encountered. Recalling that the cobalt atom is nearly octahedral[5] with bond angles close to 90° rather than 109°, we suggest that the latter conformation would force destabilizing gauche interactions between the perfluoroalkyl group and both PPh_2 phenyl groups.

Solution Conformation. ^{1}H nuclear Overhauser effect difference (NOED) spectra[43] were measured in order to establish whether the solid-state conformation was retained in solution for $(+)_{436}$-**7bα**. Comparative NOED data were also obtained for $(-)_{436}$-**7bα**, $(-)_{436}$-**7aα**, and $(+)_{436}$-**7aα**. Table V displays the quantitative NOE enhancements measured. Both Co epimers of the n-C_3F_7 (**7bα**) and CF_3 (**7aα**) series show parallel effects; hence, we propose that their solution conformations are similar. Irradiation of the Cp signal gives large positive enhancements (ca. 4–7%) for the ortho protons of the PPh_2 groups consistent with a solution conformation in which a pseudoequatorial Cp is gauche to both rings as found in the solid state of $(+)_{436}$-**7bα**. Positive OMe → Cp NOE enhancements are also expected between the Cp and OMe groups since they also define a similar gauche relationship. However, Table V shows that the measured effects are very small (ca. ≤1%) and cannot be considered diagnostic. Presumably the increased flexibility associated with the Me–O–P link increases the average distance with respect to the Cp ring and results in very low enhancements. The NOED evidence strongly supports the premise that the solid-state conformation of $(+)_{436}$-**7bα** is retained in solution. If the alternate conformation in which Cp is pseudoaxial were significantly populated, NOE enhancements would be expected between Cp and only **one** PPh_2 o-phenyl. The NOED results do not eliminate the possibility of free rotation about the Co–P(N) bond. However, we feel this is highly unlikely. Confirmation of this fact derives from an IR study which demonstrated that the ν_{NH} is not affected by dilution, showing that hydrogen bonding persists in solution.

Experimental Section

Reagents and Methods. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques.

---

(39) Day, V. W.; Tavavaiepour, I.; Abdel-Meguid, S. S.; Kirner, J. F.; Goh, L.-Y.; Muetterties, E. L. *Inorg. Chem.* **1982**, *21*, 657–663.

(40) Korp, J. D.; Bernal, I. *J. Organomet. Chem.* **1981**, *220*, 355–364.

(41) Brunner, H.; Weber, H.; Bernal, I.; Reisner, G. M. *Organometallics* **1984**, *3*, 163–170.

(42) Brunner, H. *Angew. Chem.* **1983**, *22*, 897–1012.

(43) Sanders, J. K. M.; Mersh, J. D. *Prog. Nucl. Magn. Reson. Spectrosc.* **1983**, *15*, 353–400.

Nitrogen gas was purified by passing it through a series of columns containing activated molecular sieves (3 Å), granular phosphorus pentoxide, and DEOX catalyst (100 °C). Toluene, benzene, and ether were distilled from blue solutions of sodium benzophenone ketyl. Methylene chloride was freshly distilled from P_4O_{10}. Acetone and ethyl acetate were distilled from activated 3-Å molecular sieves. The progress of reactions was monitored by analytical thin-layer chromatography (precoated TLC plates, silica gel F-254, Merck). NMR spectra were recorded on a General Electric GN300-NB spectrometer. Solution IR spectra were recorded as thin films on a Mattson Polaris FTIR instrument with 4-cm^{-1} resolution. Optical rotation measurements were determined in toluene (ca. 1 mg/mL) in a 1-cm path length cell using a Perkin-Elmer Model 241 polarimeter. CD spectra were determined in toluene (ca. 1 mg/mL) on a Jasco J 40 A apparatus using a 0.1-cm path length cell. Melting points were determined in sealed capillaries and are uncorrected. Elemental analyses were performed by Guelph Chemical Laboratories, Inc. Chromatographic separations were carried out using a Chromatotron (Harrison Associates) with 1–2-mm-thick (silica gel$_{60}$)PF$_{254}$ (Merck) adsorbant. The compounds η^5-CpCo(CO)(I_2),[44] (*S*)-(−)-PPh_2NRC*H(Me)Ph,[45] η^5-CpCo(X)(CO)(I) (**4a**,**b**[46]), and η^5-CpCo(X)(PPh_2NRCH(Me)Ph)(I) (**6aβ**, **6bα**, and **6bβ**[26]) were prepared using the established procedures. Commerical samples of trimethyl phosphite were distilled before use. Samples of CF_3I and *n*-C_3F_7I (Aldrich) were used as received.

Proton NOED spectra were determined under steady-state conditions on a GE GN300-NB instrument at 25.0 ● 0.1 °C. Data were collected using interleaved experiments of 16 or 32 transients cycled 12–16 times through the list of decoupling frequencies. In each experiment, the decoupler was gated on in continuous wave (CW) mode for 6 s with sufficient attenuation to give an approximate 70–90% reduction in intensity of the irradiated peak. A 60-s delay preceded each frequency change. A set of four equilibrating scans was employed to equilibrate the spins prior to data acquisition. No relaxation delay was applied between successive scans of a given frequency. Difference spectra were obtained on 16K or zero-filled 32K data tables which had been digitally filtered with a 0.1-Hz exponential line-broadening function. Quantitative data were obtained by integration.

Crystal Structure Determination. Intensity data were collected at room temperature on an Enraf-Nonius CAD4 (Mo K_α radiation with graphite monochromater) automated diffractometer controlled by the NRCCAD program.[47] Data were collected with profile analysis and $\Theta/2\Theta$ scan mode.

Structure Solution and Refinement. Orange prisms of $(+)_{436}$-**7bα** were grown from dilute solutions of methylene chloride/hexane at −30 °C. Unit cell dimensions for $(+)_{436}$-**7bα** were derived from 24 reflections with a 2Θ range of 20.00–28.00°. Systematic absences for the total data set were consistent with the space group $P2_1$. Structures were determined by direct methods and refined by successive cycles of least squares. All calculations were carried out using the NRCVAX suite of crystal-structure-solving programs.[48] The phenyl rings were refined as rigid groups to improve the reflections/parameters ratio. The absolute configuration for $(+)_{436}$-**7bα** was determined using the NRCVAX utility BIVOET.[35]

Carbonyl-Substitution Reactions of 4a,b. Preparation of 6(a,b)(α,β) and 8a,b. These complexes were prepared by treatment of **4a**,**b** with the appropriate P-donor ligand at room temperature in methylene chloride solvent. In a typical preparation, 0.5934 g (1.954 mmol) of (*S*)-(−)-PPh_2NHC*H(Me)Ph was added to a solution of 0.7396 g (1.651 mmol) of η^5-CpCo(*n*-C_3F_7)(CO)(I), **4b**, in 20 mL of methylene chloride and stirred at ambient temperature for 2 h. A rapid evolution of CO was observed. Removal of volatiles under oil pump vacuum left a dark solid which was purified by radial thick layer chromatography (SiO_2/ethyl acetate:hexane 1:15) to give 1.096 g (1.513 mmol, 91.7%) of η^5-CpCo(*n*-C_3F_7)(PPh_2NHC*H(Me)Ph)(I), **6bα**, as a ca. 1:1 mixture of *R*,*S*$_{Co}$ epimers. **6aα**, **6aβ**, **6bβ**, **8a**, and **8b** were prepared in a similar fashion. Analytical and spectroscopic data are reported in Tables I–III. Preparative details are summarized in Table IV.

Preparation of η^5-CpCo(X)(PNR*)(P(O)(OMe)$_2$), 7(a,b)α. A solution of 0.8037 g (1.1086 mmol) of **6b** and 0.1478 g (1.1918 mmol) of $P(OMe)_3$ in ca. 10 mL of benzene was prepared in a Carius tube and heated to 120 °C for 17 h. Removal of volatiles followed by filtration and radial thick layer chromatography (SiO_2/EtOAc:hexane 1:5) separated two orange zones. The lower R_f zone was identified as (S_{Co},S_C)-**7bα** (86.4 mg, 11.0%) on the basis of spectroscopic and crystallographic evidence. The higher R_f product (95.5 mg, 12.2%) was characterized as its Co epimer, (R_{Co},S_C)-**7bα** (cf. text).

Similarly, refluxing 0.1381 g (0.2210 mmol) of **6a** with 0.0316 g (0.2630 mmol) of $P(OMe)_3$ in benzene for 4 h gave after chromatography (SiO_2/EtOAc:hexane 1:1) (S_{Co},S_C)-**7aα** (0.0321 g, 24.3%) as a low-R_f orange zone and (R_{Co},S_C)-**7aα** (0.0360 g, 27.2%) as a high-R_f orange zone.

Reaction of 6(a,b)β with Trimethyl Phosphite. In a typical reaction, a NMR tube was charged with equimolar amounts of **6bβ** and $P(OMe)_3$ (ca. 0.01 mmol) dissolved in 0.4 mL of CD_2Cl_2. ^1H NMR spectra at ambient temperature showed that the major product was η^5-CpCo(*n*-C_3F_7)($P(OMe)_3$)(I), **8b**. Similar results were obtained for **6aβ**.

Directed Halide Substitution of η^5-CpCo(*n*-C_3F_7)(P(OMe)$_3$)(I), 8b. A solution of 0.0215 g (0.1101 mmol) of $AgBF_4$ in acetone was slowly added via syringe to a stirred solution of 0.0350 g (0.0643 mmol) of **8b** in acetone. After 0.5 h, the resulting yellow precipitate of AgI was centrifuged, and a solution of 0.0209 g (0.0655 mmol) of **6β** in acetone was added. After stirring at 20 °C for 10 min, the solvent was removed under oil pump vacuum, leaving an orange red solid (0.0475 g, 82.5%) as [η^5-CpCo(*n*-C_3F_7)(PPh_2N(Me)CH(Me)Ph)($P(OMe)_3$)]BF_4, **9bβ**.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for financial support. We are indebted to Dr. J. N. Bridson, Memorial University Crystallography Unit, for helpful discussions.

Registry No. **4b**, 12128-52-8; **6aα** (isomer 1), 142260-84-2; **6aα** (isomer 2), 142394-44-3; **6aβ** (isomer 1), 65073-89-4; **6aβ** (isomer 2), 65137-29-3; **6bα** (isomer 1), 65073-91-8; **6bα** (isomer 2), 65137-27-1; **6bβ** (isomer 1), 65073-92-9; **6bβ** (isomer 2), 65137-26-0; (S_{Co},S_C)-**7aα**, 142260-87-5; (R_{Co},S_C)-**7aα**, 142393-00-8; (S_{Co},S_C)-**7bα**, 142293-83-2; (R_{Co},R_C)-**7bβ**, 142394-45-4; **8a**, 142260-85-3; **8b**, 142260-86-4; **9bβ**, 142260-89-7; (*S*)-(−)-PPh_2NHC*H(Me)Ph, 71554-93-3.

Supplementary Material Available: Tables of atomic and thermal parameters, anisotropic temperature factors, and bond distances and angles (13 pages). Ordering information is given on any current masthead page.

OM921175N

---

[44] King, R. B. *Inorg. Chem.* **1966**, *5*, 82–87.

[45] Brunner, H.; Doppelberger, J. *Chem. Ber.* **1978**, *111*, 673–691.

[46] King, R. B.; Treichel, P. M.; Stone, F. G. A. *J. Am. Chem. Soc.* **1961**, *83*, 3593.

[47] LePage, Y.; White, P. S.; Gabe, E. J. NRCCAD-An Enhanced CAD4 Control Program. Presented at the American Crystallography Association Annual Meeting 1986; p 24.

[48] Gave, E. J.; Le Page, Y.; Charland, J. P.; Lee, F. L.; White, P. S. *J. Appl. Crystallogr.* **1989**, *22*, 384–387.