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Optically Active Transition-Metal Compounds.[1,2] Preparation, Structure, Absolute Configuration, and Conformational Analysis of Chiral Pseudooctahedral Cobalt(III) Phosphonato and Phosphinato Complexes. Optical Induction in the Transition-Metal Arbuzov Reaction

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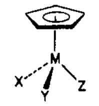
(S)-η^5-CpCoI$_2$(PPh$_2$NHCH(Me)Ph) reacts with 1 equiv of trimethyl phosphite or dimethyl phenylphosphonite in benzene or methylene chloride solution to give diastereomeric Arbuzov products (R,S_{Co},S_C)-η^5-CpCoI(PPh$_2$NHCH(Me)Ph)(P(O)(OMe)$_2$) (**6a,b**) and (R,S_{Co},R,S_P,S_C)-η^5-CpCoI(PPh$_2$NHCH(Me)Ph)(PhP(O)(OMe)) (**7a–d**), respectively. Compounds **6a** and **7a** were characterized by X-ray diffraction, including determination of absolute configuration. **6a** crystallizes in the space group $P2_12_12_1$ with a = 9.470 (2) Å, b = 15.136 (3) Å, c = 19.562 (4) Å, and Z = 4 and was refined to R = 0.041 for 4721 reflections. **7a** also crystallizes in $P2_12_12_1$ with a = 9.995 (2) Å, b = 13.934 (2) Å, c = 22.422 Å, and Z = 4 and was refined to R = 0.058 for 3749 reflections. The absolute configuration of all diastereomers was established by a combination of crystallographic, circular dichroism, and epimerization studies. Conformational analysis on the basis of crystallographic data in the solid state and proton nuclear Overhauser difference (NOED) spectra in solution show a quasi-chair conformation determined by the presence of a strong intramolecular NH···O=P hydrogen bond. Initial substitution of diastereotopic iodide occurs with essentially zero optical yield; however, considerable chiral induction occurs in the subsequent Arbuzov dealkylation step leading to the phosphinato complexes 7.

Introduction

The cyclopentadienyl complexes η^5-CpMXYZ (1, X, Y, Z = 2e donor ligands) are a rich source of chiral transition-metal atoms[3] with pseudooctahedral[4,5] geometry, in which η^5-Cp is considered to occupy three *fac* sites of an approximate octahedron.



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Extensive applications of the complexes 1 (X = prochiral substrate), which employ a chiral transition-metal atom as the source of molecular asymmetry, as chiral synthons for stoichiometric, stereoselective synthesis have been reported by Davies[6] and others.[7] Accordingly, these complexes continue to serve as a focal point for the elucidation of the fundamental factors determining chiral stability at the transition-metal atom and conformational preferences that ultimately determine the efficiency of chiral information transfer.[8]

Configurational stability at the chiral transition-metal atom of 1 in solution is a function of the ligand sphere.[3,9,10] Among metals with formal oxidation state +3, cobalt provides both relatively stable (1, XY = bidentate Schiff base, Z = perfluoroalkyl[11,12]) and labile (1, XY = bidendate Schiff base, Z = halide, pseudohalide, phosphine;[12] 1, X = perfluoroalkyl, Y = iodide, Z = PPh$_2$N(Me)C*H(Me)-Ph;[13] 1, XY = η^2-C$_2$H$_5$, Z = PMe$_2$Ph[14]) examples.

This study was undertaken in order to prepare additional chiral examples of type 1 and to determine the configurational stability/lability at cobalt. Herein we report the preparation, characterization, resolution, and absolution configuration of a series of diastereomeric phosphonato and phosphinato Co(III) complexes 1 (X =

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Table I. IR Data[a]

compd	ν_{NH}, cm^{-1}	$\nu_{P=O}$, cm^{-1}	ν_{P-OC}, cm^{-1}	ν_{PO-C}, cm^{-1}	other, cm^{-1}
4	3360 (b)				3060 (w), 3030 (w), 2970 (w), 2925 (w), 1434 (m), 1416 (m), 1203 (m), 1118 (m), 1097 (m), 1032 (w), 1014 (w), 1000 (w), 962 (w), 691 (m), 563 (w), 532 (m), 508 (w), 476 (w)
6a	3120 (b)	1147 (s)	1040 (s), 1011 (s)	693 (s)	3060 (w), 2970 (w), 2940 (w), 2885 (w), 1545 (m), 1436 (m), 1205 (w), 1120 (w), 1098 (m), 580 (m), 560 (w), 529 (w), 481 (w)
6b	3120 (b)	1147 (s)	1039 (s), 1009 (s)	698 (s)	3060 (w), 2970 (w), 2838 (w), 1545 (w), 1438 (m), 1205 (w), 1122 (w), 1100 (m), 580 (m), 531 (m), 506 (w), 482 (w)
7a	3120 (vb)	1134 (s)	1008 (s)	685 (s)	3060 (w), 3025 (w), 2980 (w), 2940 (w), 2835 (w), 1535 (w), 1480 (w), 1435 (m), 1095 (s), 1205 (w), 559 (m), 530 (m), 483 (w), 454 (w)
7b	3120 (vb)	1133 (s)	1005 (s	695 (s)	3060 (w), 3025 (w), 2980 (w), 2940 (w), 2870 (w), 2835 (w), 1545 (w), 1482 (w), 1435 (m), 1204 (w), 1094 (s), 564 (m), 530 (m), 482 (w), 455 (w)

[a] Ca. 5 mg/mL in CCl_4. Abbreviations: b, broad; vb, very broad; s, strong; w, weak; m, medium. ±3 cm^{-1} except for ν_{NH} (±10 cm^{-1}).

iodide, Y = (*S*)-(−)-$PPh_2NHCH(Me)Ph$, *Z* = $P(O)(OR)_2^-$, $P(O)R(OR)^-$) with exceptional configurational stability at cobalt.

Results and Discussion

Preparation and Characterization of the Phosphonato Compounds 6a,b. Treatment of deep purple solutions of (*S*)-η^5-$CpCoI_2(PPh_2NHCH(Me)Ph)$ (**4**) with 1 equiv of trimethyl phosphite in benzene or methylene chloride at ambient temperature rapidly affords a brown solution which slowly turns green-yellow. Column chromatography and fractional crystallization of the crude, green product separates an approximate 1:1 ratio of higher R_f less soluble $(+)_{436}$-**6a** and lower R_f more soluble $(-)_{436}$-**6b** diastereomers which are epimeric at cobalt. The dark green, air-stable dimethyl phosphonato complexes are configurationally stable in solution. ^1H NMR analysis indicates a half-life for cobalt epimerization in the order of 150 h at 298 K in toluene-d_8.

$$\underset{\mathbf{3}}{\mathrm{CpCoI_2(CO)}} \xrightarrow{\mathrm{P^*}} \underset{\mathbf{4}}{\mathrm{CpCoI_2P^*}} \xrightarrow{\mathrm{P(OMe)RR}}$$

$$\underset{\mathbf{5}}{\mathrm{[CpCoIP^*P(OMe)RR]^+I^-}} \xrightarrow{-\mathrm{MeI}} \mathrm{CpCoIP^*P(O)RR}$$

$$\mathbf{6a,b}\text{: } \mathrm{RR = (OMe)_2}$$

$$\mathbf{7a\text{–}d}\text{: } \mathrm{RR = Ph(OMe)} \qquad (1)$$

$$\mathrm{P^* = (\mathit{S})\text{-}(-)PPh_2NHCH(Me)Ph} \quad (2)$$

Presumably the reaction proceeds (cf. eq 1) by initial substitution of diastereotopic iodide to produce a labile, chiral, cationic phosphite intermediate[15-21] **5**[22] which subsequently dealkylates via a Michaelis–Arbuzov like rearrangement[12,15,17,23-27] to afford the isolated dimethyl phosphonato complexes **6a,b**. ^1H NMR analysis of the reaction solutions shows that the dealkylation is quantitative and that the ratio of diastereomers **6a**:**6b** is approximately 1:1. The driving force for the dealkylation can be attributed to the formation of a very stable phosphoryl P=O bond which provides a thermodynamic sink in the order of 272 kJ/mol.[28] Free halide ion is apparently required for the rearrangement since stable phosphite complexes are isolated in cases where a ligand other than halide is displaced.[15,29,30] Dealkylation via intramolecular attack of other nucleophiles can also lead to phosphonato products.[31] A parallel for the organometallic Arbuzov rearrangement of coordinated phosphite is found in the halide-induced dealkylation of oxycarbenes to acyls.[30]

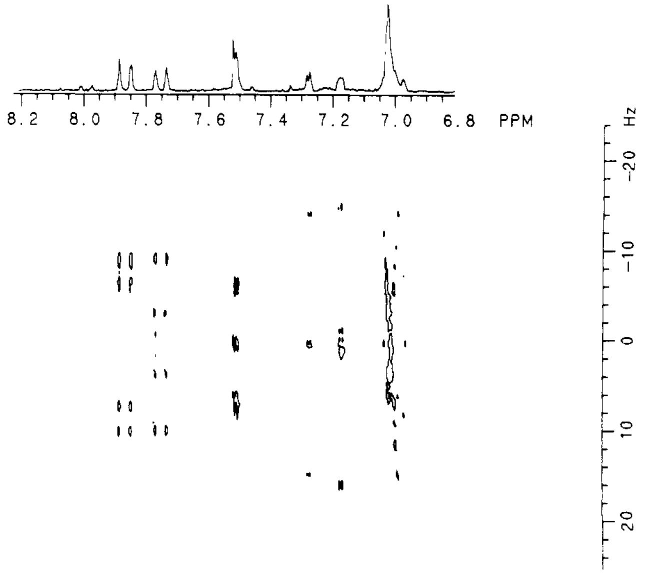

Figure 1. Typical two-dimensional *J*-resolved ^1H NMR spectrum showing residual heteronuclear couplings (**6b** in CD_2Cl_2).

The diastereomeric dimethyl phosphonato complexes **6a,b** are characterized unambiguously by their analyses, field desorption mass spectra (FDMS) (cf. Experimental Section), IR spectra (cf. Table I), and NMR spectra (cf. Tables II and III). Both **6a,b** show nearly identical FDMS with a molecular ion at *m/e* 665 as well as major fragments at *m/e* 556 and 429 corresponding to the sequential loss of $P(OMe)_2^{\bullet}$ and $I^{\bullet}$, respectively.

Solution IR spectra in CCl_4 (cf. Table I) show a strong P=O stretch at 1147 cm^{-1}, significantly lower frequency

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

compd	δ(NPPh) [δ(OPPh)] ortho[b]	δ(NPPh) δ(OPPh) meta para	δ(C*Ph)	δ(NH)[c]	δ(Cp)	δ(OMe)	δ(C*H)	δ(C*Me)
4	8.07 7.78	7.57 7.54 7.22 7.33	7.04 (m)	2.96 (16.6, 10.7)	5.01 (s)		3.96 (9.6, 9.6, 6.6)[d]	1.13 (d, 6.6)
6a	7.98 (10.6) 7.47 (10.8)	7.21 (2) 7.58 (<1) 7.12 (2) 7.55 (<1)	6.99 (m)	6.28 (15.3, 9.7)	4.90 (s)	3.82 (d, 10.0) 3.68 (d, 11.1)	3.74 (9.7, 9.7, 6.7)[d]	1.23 (d, 6.7)
6b	7.86 (10.6) 7.75 (10.8)	7.28 (2) 7.54 (<1) 7.18 (2) 7.52 (<1)	7.00 (m)	6.10 (15.0, 6.8)	4.89 (s)	3.83 (d, 10.0) 3.66 (d, 11.1)	3.96 (10.1, 7.7, 6.7)[e]	1.19 (d, 6.7)
7a	8.03 (11.7) 7.94 (10.9) [7.63 (11.7)]	7.49[f] 7.18[f]	6.99 (m)	6.94 (13.7, 9.6)	4.74 (s)	3.61 (d, 10.5)	3.81 (9.3, 9.3, 6.7)[d]	1.29 (d, 6.9)
7b	[7.93 (10.5)] 7.89 (10.9) 7.86 (10.9)	7.55[f] 7.46[f] 7.29[f] 7.19[f] 7.70[f]	7.08 (m)	6.82 (13.8, 8.1)	4.75 (s)	3.63 (d, 10.5)	3.99 (10.8, 8.2, 6.6)[e]	1.16 (d, 6.6)
7c[g]	7.97 (nm) 7.58 (nm)[h,f]	7.51[f] 7.40[f] 7.24[f] 7.1[f]	7.1 (m)	5.55 (15.5, 9.6)	4.70 (s)	3.49 (d, 10.9)	3.94 (nm)[d]	1.27 (d, 6.6)
7d[g]	8.14 (nm) 7.90 (nm) 7.69 (nm)[f]	7.47[f] 7.17[f]	7.14 (m)	5.49 (17.0, 9.9)	4.74 (s)	3.53 (d, 10.9)	3.99 (nm)[d]	1.14 (d, 6.7)

[a] 300.1 MHz; chemical shifts in ppm relative to internal TMS; J values in Hz; solvent = CD_2Cl_2; ca. 2–4 mg/mL. Abbrevations: nm, not measured; m, multiplet; s, singlet; d, doublet. [b] Second-order AA′BB′CX multiplets (J_{HH}). [c] Doublet of doublets ($^2J_{PH}$, $^3J_{PH}$). [d] 1:3:2:3:6:1:1:6:3:2:3:1 triplet of quartets ($^3J_{PH}$, $^3J_{NHH}$, $^3J_{HH}$). [e] 1:3:1:1:3:3:3:1:1:3:3:3:1:1:3:1 quartet of quartets ($^3J_{PH}$, $^3J_{NHH}$, $^3J_{HH}$). [f] Definitive assignments not possible. [g] 250 MHz; solvent = $CDCl_3$. [h] Two nonequivalent sets of ortho protons.

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

compd	δ(NPC_6H_5) or [δ(OPC_6H_5)] ipso ortho meta para	δ(CC_6H_5) ipso ortho meta para	δ(Cp)	δ(OMe)	δ(C*H)	δ(C*Me)
4	134.62 (d, 10.4), 133.74 (d, 10) 128.29 (d, 10.2), 127.80 (d, 10.7) 133.30 (d, 9.5), 133.03 (d, 9.7) 131.39 (d, 2.5), 130.97 (d, 2.5)	145.25 125.70 128.06 126.37	86.64 (d, 3.3)		54.89 (d, 10.5)	26.34 (d, 4.9)
6a	137.39, 136.63 127.84 (d, 10.4), 127.34 (d, 9.9) 133.93 (d, 9.4), 132.09 (d, 10.7) 130.76 (d, 3), 130.34 (d, 3)	146.68 125.87 127.65 125.80	89.23 55.41 (d, 10.1)	54.04 (d, 10.8)	51.05 (d, 10.1)	26.98 (d, 5.2)
6b	137.58, 136.76 127.73 (d, 10) 133.55 (d, 10.7), 132.11 (d, 8.7) 131.04 (d, 3), 129.91 (d, 3)	145.68 126.13 127.74 125.82	89.06 54.61 (d, 9.6)	55.4 (d)	51.14 (d, 10)	26.72 (d, 8.0)
7a	138.14, 137.35, [134.59] 127.43 (d, 10.2), 127.67 (d, 10.2), [127.83 (d)][b] 134.21 (d, 9.5), 132.40 (d, 10.6), [129.82 (d, 5.1)][b] 130.94, 130.78, [129.82][b]	147.87 126.23 127.70 125.73	88.98	55.53 (d, 10.3)	51.61 (d, 10.5)	26.84 (d, 8.2)
7b	137.98, 137.27, [134.53][b] 128.90 (d, 9.8), 127.52 (d, 10.5), [127.57 (d)][b] 133.92 (d, 9.9), 132.49 (d, 10.3), [130.95 (d, 9.2)][b] 130.68, 130.36, [129.81][b]	146.29 126.01 127.70 125.81	89.04	53.96 (d, 11.3)	51.77 (d, 10.6)	26.94 (d, 4.7)

[a] 75.5 or 62.9 MHz, in $CDCl_3$, chemical shifts reported in ppm relative to internal TMS; J values in Hz. [b] Assignments ambiguous.

than that reported for related dialkyl phosphonato iron[15] (1159–1180 cm^{-1}) or nickel[33] (1150 cm^{-1}) complexes. The decreased P=O force constant and the very large, concentration independent, bathochromic shift observed for the N—H stretch of compounds **6a,b** (cf. Table I) compared to the parent compound **4** strongly suggest the presence of an intramolecular N—H···O=P hydrogen bond in solution[34,35] which is confirmed in the solid state by crystal data (vide infra).

The ^{1}H NMR spectra of the dimethyl phosphonato complexes **6a,b** (cf. Tables II and III) show distinct η^5-Cp,

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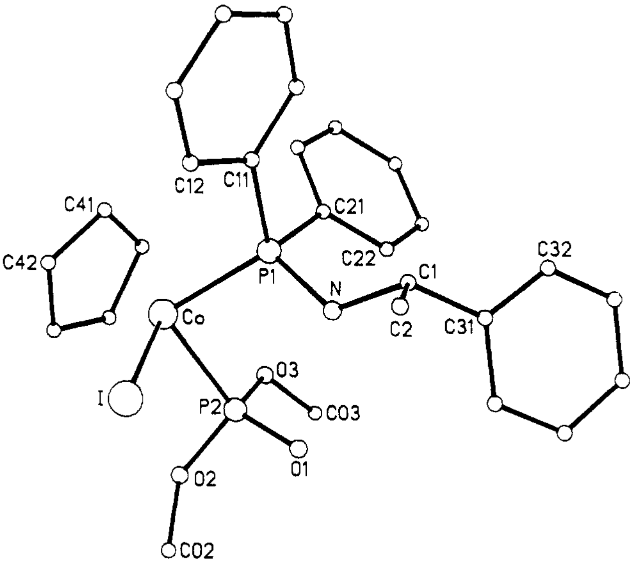

Figure 2. Molecular geometry and absolute configuration of **6a**.

NH, C*H*PhMe, and CHPh*Me* resonances typical for diastereomeric "piano-stool" complexes.[3] The diastereotopic OMe groups appear as pairs of doublets at 3.82 and 3.68 ppm for **6a** and 3.83 and 3.66 ppm for **6b**. Consistent with the presence of a strong, intramolecular NH···O═P hydrogen bond, the chemical shift of the aminophosphine NH is both concentration and solvent independent and is strongly deshielded in **6a,b** (δ 6.28, 6.10) compared to that in **4** (δ 2.96).[36] The NP*Ph* ortho protons were assigned on the basis of two-dimensional ^{1}H J-resolved spectra that retain heteronuclear scalar couplings in the F1 dimension (cf. Figure 1). At 300 MHz, two doublets ($^3J_{PH}$ = 10–11 Hz) corresponding to the two diastereotopic phenyl groups are observed for each of **6a,b**. Second-order effects leading to artifacts in the F1 projection obviated definitive assignments of the meta and para protons.

Solid-State Structure, Chiroptical Properties, and Absolute Configuration of 6a,b. An X-ray structure (cf. Figure 2), determined on a single crystal of the $(+)_{436}$-**6a** diastereomer obtained from toluene/hexane, confirmed a "piano-stool" structure with a central cobalt atom coordinated to iodide, aminophosphine, and phosphonate ligands. I–Co–P(1), I–Co–P(2), and P(1)–Co–P(2) bond angles all approach 90° as found for related isostructural complexes.[5,37–40] Accordingly, the coordination geometry of **6a** is best described as distorted octahedral (cf. structure **2**) with η^5-Cp occupying three *fac* coordination sites (cf. Figure 2 and Table IV). Although Tolman's *X* parameter,[41] ^{13}C NMR data,[42] NQR data,[43] and crystal data[37,44] suggest that the ligand σ-donor/π-acceptor ability decreases along the series $Ar_2PNR > P(OR)_3 > P(O)(OR)_2^-$, the aminophosphine Co–P bond in **6a** (221.1 pm) and the dimethyl phosphonato Co–P bond (219.9 pm) are effectively equal in the present case. Presumably the lack of appreciable bond length variation reflects a greater steric demand of the diphenylaminophosphine ligand. All Co–η^5Cp bond distances are ordinary and approximately equal with an average value of 208.9 (28) pm and a range of 207.4–212.8 pm. A distorted tetrahedral geometry[30,37,44] consistent with an opening of the Co—P═O bond angle (120.6°) and a concomitant closing of the Co–P–O angles (109.0 and 104.0°) is found for the dimethyl phosphonato ligand in **6a**. A strong intramolecular hydrogen bond is evident from the proximity of the aminophosphine NH and the basic phosphoryl oxygen atom.[45] Refinement with an idealized (96 pm) N–H bond distance gives values for the H···O bond distance (197 pm) and N···O bond distance (287 pm) which are well within the range considered diagnostic for hydrogen bonded N—H···O.[46]

Table IV. Atomic Coordinates ($\times 10^4$) and Isotropic Temperature Factors (pm^2 $\times$ 10^{-1}) for 6a

atom	*x*	*y*	*z*	U^a
I	6426 (1)	4346 (1)	2625 (1)	55 (1)
Co	4731 (1)	5653 (1)	2807 (1)	35 (1)
P(1)	3693 (1)	5574 (1)	1797 (1)	34 (1)
P(2)	3130 (2)	4784 (1)	3266 (1)	45 (1)
O(1)	2695 (4)	3955 (2)	2917 (2)	59 (1)
O(2)	3588 (8)	4559 (4)	4047 (3)	79 (3)
C(O2)	4138 (8)	3712 (4)	4221 (3)	79 (3)
O(3)	1854 (3)	5417 (2)	3416 (2)	52 (1)
C(O3)	519 (7)	5099 (4)	3666 (4)	92 (3)
C(11)	4695 (5)	6005 (3)	1067 (2)	40 (2)
C(12)	6110 (5)	5809 (4)	1020 (3)	63 (2)
C(13)	6895 (7)	6067 (4)	466 (3)	76 (2)
C(14)	6297 (6)	6537 (4)	−59 (3)	64 (2)
C(15)	4902 (6)	6744 (3)	−20 (3)	61 (2)
C(16)	4095 (6)	6482 (3)	543 (2)	50 (2)
C(21)	2063 (5)	6205 (3)	1775 (2)	39 (2)
C(22)	774 (5)	5771 (3)	1836 (2)	46 (2)
C(23)	−485 (6)	6229 (4)	1851 (3)	58 (2)
C(24)	−475 (6)	7149 (4)	1824 (3)	59 (2)
C(25)	768 (5)	7591 (3)	1781 (3)	52 (2)
C(26)	2041 (5)	7140 (3)	1750 (3)	44 (2)
C(31)	1381 (6)	3863 (3)	900 (2)	44 (2)
C(32)	328 (7)	4152 (4)	481 (3)	62 (2)
C(33)	−1002 (7)	3789 (5)	491 (3)	83 (3)
C(34)	−1304 (8)	3114 (5)	920 (3)	87 (3)
C(35)	−288 (8)	2794 (4)	1339 (3)	86 (3)
C(36)	1038 (7)	3172 (4)	1346 (3)	72 (2)
C(41)	5391 (6)	6971 (3)	2668 (3)	56 (2)
C(42)	6478 (6)	6501 (3)	3000 (3)	54 (2)
C(43)	5936 (6)	6155 (3)	3606 (3)	53 (2)
C(44)	4532 (6)	6438 (3)	3671 (3)	47 (2)
C(45)	4163 (5)	6920 (3)	3076 (2)	45 (2)
N	3319 (4)	4556 (2)	1560 (2)	43 (2)
C(1)	2830 (5)	4263 (3)	883 (2)	50 (2)
C(2)	3932 (7)	3627 (4)	581 (3)	82 (3)
NH	2958	4361	1968	52

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

In spite of apparent strong intramolecular hydrogen bonding the phosphoryl P═O bond distance is shorter (148.5 pm) than the P—OMe bond distances (162.5, 157.0 pm) but within the range reported for examples with[30,37] and without[44] secondary bonding interactions to electrophilic centres.

The absolute configuration of both chiral atoms in **6a** was determined from the crystal data by using Rogers' η method.[47] The absolute configuration of the chiral am-

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Table V. Selected Bond Distances (pm) and Bond Angles (deg) for 6a and 7a

6a				7a			
bond dist		bond angle		bond dist		bond angle	
I–Co	257.2 (1)	I–Co–P(1)	96.4 (1)	I–Co	256.5 (2)	I–Co–P(2)	94.1 (2)
Co–P(2)	219.9 (1)	I–Co–P(2)	91.5 (1)	Co–P(1)	221.7 (3)	I–Co–P(1)	93.0 (2)
Co–P(1)	221.1 (1)	P(1)–Co–P(2)	91.5 (1)	Co–P(2)	222.0 (3)	P(1)–Co–P(2)	89.2 (2)
P(2)–O(1)	148.5 (3)	Co–P(2)–O(1)	120.6 (3)	P(1)–O(1)	149.9 (6)	Co–P(1)–O(1)	117.0 (3)
P(2)–O(3)	157.0 (3)	O(1)–P(2)–O(2)	109.2 (3)	P(1)–O(2)	161.0 (6)	O(1)–P(1)–O(2)	112.2 (4)
P(2)–O(2)	162.5 (3)	Co–P(2)–O(2)	109.0 (3)			Co–P(1)–C(51)	113.3 (4)
N···O(1)	287.0	Co–P(2)–O(3)	104.0 (3)	N···O(1)	277	Co–P(1)–O(2)	103.0 (3)
N–P(1)	164.8 (4)	O(2)–P(2)–O(3)	99.0 (3)	N–P(2)	166.8 (7)	C(51)–P(1)–O(1)	108.1 (4)
N*H*···O(1)	197.0	O(1)–P(2)–O(3)	112.8 (3)	N*H*···O(1)	208	C(51)–P(1)–O(2)	102.2 (4)

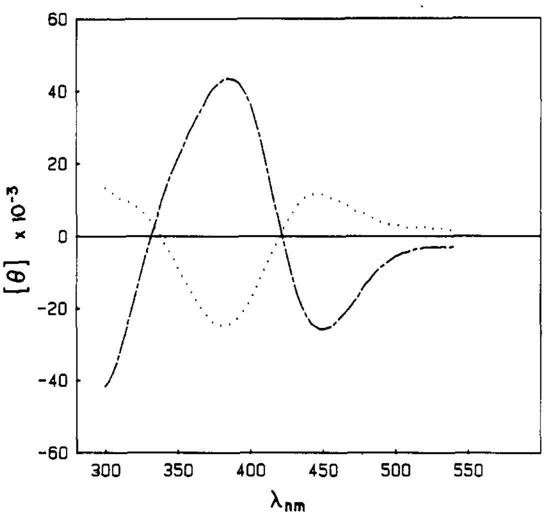

Figure 3. Circular dichroism (CD) spectra of $(+)_{436}$-**6a** (---) and **6b** (···).

inophosphine carbon was known to be *S* and thus provided an internal check of the assigned cobalt atom chirality (cf. Figure 2). With the assumption that the ligand priority sequence is I > η^5-Cp > P(O)(OMe)$_2$ > Ph$_2$PNHCH(Me)Ph, the absolute configuration at the cobalt atom in **6a** is specified as *S*[3,48] in the CIP[49] *R,S* system conventionally applied to chiral piano-stool complexes with distorted tetrahedral geometry. Thus **6a** has the absolute configuration S_{Co},S_C.[50]

The CD spectra of $(+)_{436}$-**6a** and $(-)_{436}$-**6b** are quasi-mirror images (cf. Figure 3). Since the chiral transition-metal atom generally dominates chiroptical properties,[3] the CD spectra demonstrate that **6a** and **6b** are epimeric at cobalt with absolute configurations S_{Co},S_C and R_{Co},S_C, respectively.[50]

Solid-State Conformation of 6a. Figure 4 shows ORTEP drawings of the Newman projections along the PN–Co, P(O)–Co, and P–N bonds which demonstrate that an approximate staggered conformation is adopted in each case in the solid state. Inspection of Figure 4c reveals a quasi-chair six-membered ring formed as a result of the strong intramolecular NH···O=P hydrogen bonding. A strikingly similar 1,6 intramolecular hydrogen bond and solid-state conformation has been reported for (S_{Fe},S_C)-η^5-CpFe(CO)(C(O)Me)Ph2PNCH(Me)Ph.[51] In both hydrogen-bonded complexes the aminophosphine nitrogen and C_m (C_m = η^5-Cp centroid) are trans while related aminophosphine complexes not constrained by intramolecular hydrogen bonding prefer a gauche relationship.[52]

Varying degrees of planarity have been found for the nitrogen atom in aminophosphine complexes. Projection of the H–N–C* angle onto the plane orthogonal to the P–N bond provides a convenient assay of trigonal-planar (180°) vs pyramidal (120°) character. **6a** gives a value of ca. 142°, just outside the range of 145–173° found for related diphenyl((1-phenylethyl)amino)phosphine complexes.[52] Although theoretical[53] and structural evidence[54] correlates aminophosphine nitrogen geometry with torsional angles, **6a** is incorrectly predicted to be planar and appears to be an exception. In the present case the pyramidal nitrogen may simply be a response to the steric demands of bulky *axial* iodide.

Solution Conformation of 6a,b. Proton nuclear Overhauser difference (NOED) spectroscopy[12,55] proved invaluable in determining the solution conformation of complexes **6a,b**. Since spectroscopic results argue for retention of intramolecular hydrogen bonding in solution, the NOED spectra obtained for **6a** (cf. Figure 5) are interpreted on the basis of Figure 6 which retains the quasi-chair ring conformation observed in the solid state. The results strongly suggest conformation A (Figure 6), with *equatorial* η^5-Cp gauche with respect to an *axial/equatoral* pair of diastereotopic aminophosphine phenyl *and* phosphonate methoxy groups, as the low energy conformer. Accordingly, positive NOEs are observed for *both* sets of diastereotopic aminophosphine *o*-phenyl protons on irradiation of the η^5-Cp resonance. A weaker, but nevertheless positive, enhancement was found in the case of the more conformationally mobile methoxy groups. The reverse experiments in which the P(O)(O*Me*)$_2$ groups are irradiated (Figure 5c,e) confirm the results showing a positive enhancement for the η^5-Cp signal in both cases. Irradiation of the aminophosphine C**H* resonance (Figure 5d) identifies all the proximal *o*-phenyl protons as well as the C**Me* group. Irradiation at C*H*Me*Ph (cf. Figure 5f) identifies C**H*(Me)Ph, C*H(Me)*Ph*, NH, and *one* set of diastereotopic ortho NP*Ph*$_2$ protons (cf. Figure 4b) as proximal. Conformation B, which is not appreciably populated in

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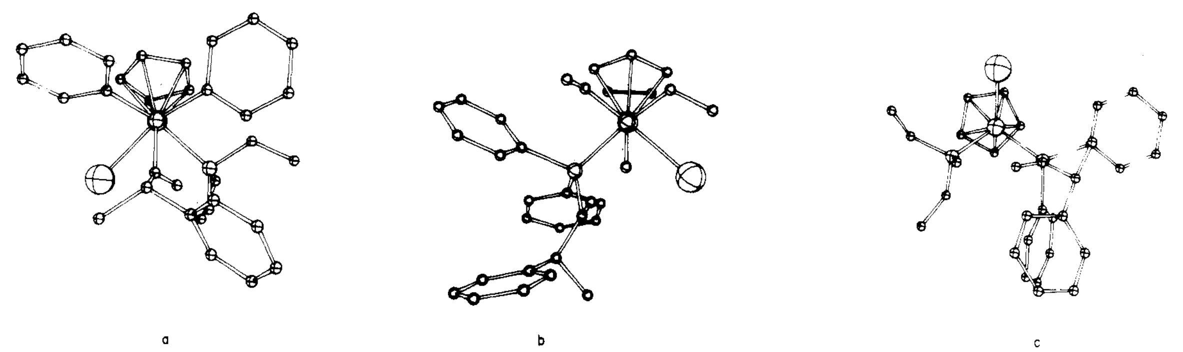


Figure 4. ORTEP drawings of Newman projections for **6a**.

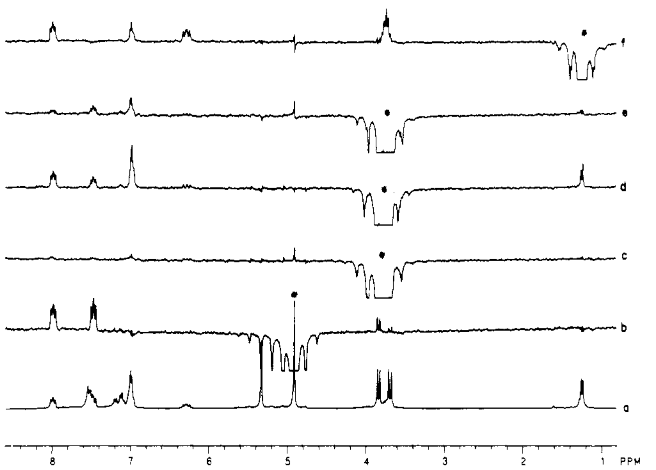


Figure 5. Proton NOED spectra for **6a**: (a) reference spectrum; (b–f) difference spectra (64X) for irradiation at the indicated asterisk (*) frequency; (b) η^5-Cp; (c) OMe; (d) C*H*Me; (e) OMe; (f) CH*Me*.

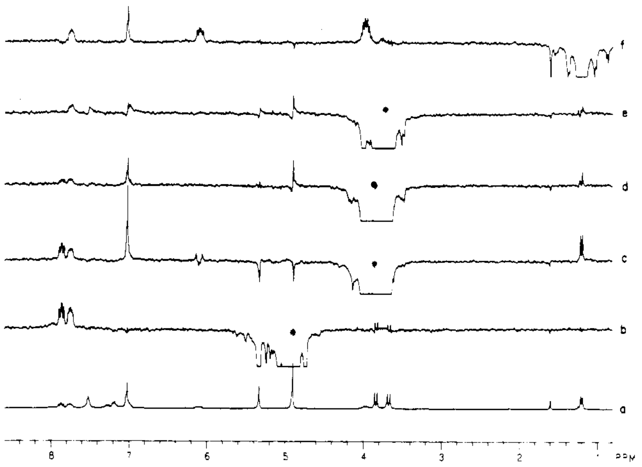


Figure 7. Proton NOED spectra for **6b**: (a) reference spectrum; (b–f) difference spectra (128X) for irradiation at the indicated asterisk (*) frequency; (b) η^5-Cp; (c) C*H*Me; (d) OMe; (e) OMe; (f) CH*Me*.

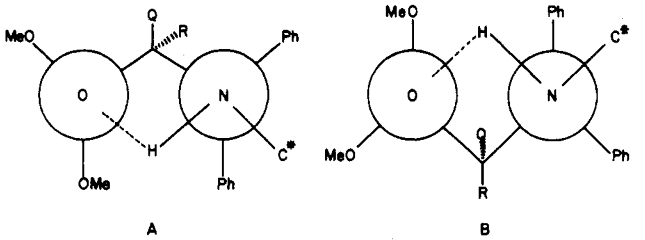


Figure 6. Solution conformation for **6**: **6a**, Q = I, R = η^5-Cp; **6b**, Q = η^5-Cp; R = I.

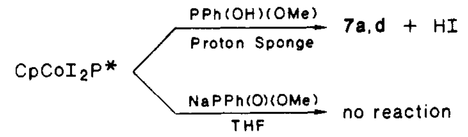
solution or in the solid state, benefits only partially from phenyl–cyclopentadienyl stabilizing interactions[12,39] since it places η^5-Cp axial and thus establishes gauche/trans interactions with *o*-NP*Ph*$_2$ and P(O)(O*Me*)$_2$.

Proton NOED spectra of the $(-)_{436}$-**6b** (cf. Figure 7) paralleled the results obtained for **6a**. Irradiation of the η^5-Cp resonance gave positive NOES at both sets of diastereotopic NP*Ph*$_2$ and P(O)(O*Me*)$_2$ groups (cf. Figure 7b). It follows that **6b** selectively populates B (cf. Figure 6), the same relative solution conformation as **6a** with pseudoequatorial η^5-Cp and two stabilizing gauche-phenyl interactions, as the low energy conformation.

Preparation and Characterization of the Phosphinato Compounds. Dialkyl phosphonites also afford Arbuzov products on treatment with **4** (cf. eq 1). Reaction of methylene chloride or benzene solutions of **4** with 1 equiv of dimethyl phenylphosphonite rapidly gives a brown solution that slowly turns green-yellow. Under Arbuzov conditions two chiral centres (Co, P) are formed; hence four diastereomeric phosphinates are possible. Thin-layer chromatography of the crude product mixture showed the formation of four green products, **7a–d** (in order of decreasing R_f values). There is considerable optical induction in the formation of the chiral phosphorus centre. Analysis of the OMe region of the proton NMR spectrum of the crude product indicated that **7a**:**7b**:**7c**:**7d** form in a 9.2:11.2:1.0:1.4 ratio after 1-h reaction time in methylene chloride. If, as found for **6a** and **6b**, the initial substitution at prochiral cobalt takes place with effectively zero optical yield, considerable optical induction must occur on dealkylation of prochiral phosphorus. Diastereomers **7a** and **7b** also dominate the thermodynamic product distribution. Although stereoisomerization does slowly occur in solution, the products are sufficiently stable to allow isolation of all four diastereomers by a combination of fractional crystallization and chromatography. Differential solubility is marked in some solvents, and nearly pure **7b** can be obtained simply by cooling acetone solutions of the crude reaction mixture. Isolation of the thermodynamically less stable, minor components **7c,d** proved troublesome as isomerization appeared to be subject to acid catalysis.

In an attempt to overcome difficulties relating to the low yield of **7c** and **7d**, **4** was reacted with methyl phenylphosphonate, PhP(OH)(OMe), in the presence of Proton Sponge (cf. eq 2). Although the tautomeric phosphinate form dominates, we reasoned that a small equilibrium concentration of racemic PhP(OH)(OMe) would substitute prochiral iodide on **4** to afford the intermediate phosphonate **8** without appreciable optical induction. Subsequent, selective deprotonation in the presence of a proton acceptor forms the phosphoryl link with retention at phosphorus and thus a near statistical product distribution.

Unfortunately the reaction requires extended reflux in benzene, and some configurational isomerism occurs.



(2)

Nervertheless, NMR analysis of the crude reaction mixture after 14-h reflux indicated that the phosphinate products were present in the ratio **7a**:**7b**:**7c**:**7d** = 5.6:5.7:1:1.6, representing a considerable improvement in the relative yield of the minor components compared to eq 1. Paradoxically, direct displacement of iodide in **4** by racemic sodium methyl phenylphosphonate in tetrahydrofuran did not appear to afford **7** (cf. eq 2).

FDMS confirmed the isomeric nature of **7a**–**d**. All diastereomers showed a molecular ion at *m*/*e* 711. Solution infrared spectra were characterized by the presence of a strong $\nu_{P=O}$ at ca. 1135 cm^{-1} (cf. Table I). The decreased stretching frequency compared to other alkyl arylphosphinate complexes[15] can be attributed to a secondary bonding interaction at the basic phosphoryl oxygen. As found for the dialkyl phosphonato derivatives, the frequency of ν_{NH} in **7** is decreased and broadened as compared to that **4**, indicating the presence of an intramolecular NH···O=P hydrogen bond which was confirmed in the solid state (vide infra).

All four products **7a**–**d** showed distinct NMR spectra (cf. Tables II and III) consistent with their formulation as diastereomeric phosphinato complexes. Two-dimensional proton J-resolved spectra of the phenyl region (cf. Figure 1) enabled partial assignment of the ortho protons of P(O)*Ph* and the diastereotopic NP*Ph*$_2$ groups in **7a**,**b**. As found for **6a**,**b**, strong intramolecular hydrogen bonding considerably deshields the NH resonance compared to that in **4**. The methoxy groups appears as a well-resolved doublet at ca. 3.5–3.6 ppm and provides for optimal quantitative analysis of the diastereomer distribution.

Solid-State Structure, Chiroptical Properties, and Absolute Configuration of 7a–d. Single cyrstals of the highest R_f isomer, (+)$_{436}$-**7a**, were obtained by fractional crystallization of a chromatographed sample from toluene/hexane. X-ray crystallography (cf. Tables VI and VII and Figure 8) confirmed a piano-stool structure with η^5-Cp, iodo, diphenyl(1-phenylethyl)amino)phosphine, and methyl phenylphosphinato ligands. Interligand bond angles about cobalt approach 90° (cf. Table V) and are consistent with a distorted octahedral geometry. The aminophosphine Co–P and phosphinato Co–P bond lengths are identical within experimental error (222.0 (3) and 221.7 (3) pm, respectively). Both are slightly longer than the corresponding bonds in **6a**. The average Co–η^5-Cp distance is 207.7 (27) pm with a range of 203.2–210.0 pm. Characteristically[30,37,44] a distorted tetrahedral geometry with an opened Co—P=O bond angle (117.0 (3)°) and a concomitant adjustment of the Co–P–OR angle to 103.3 (3)° is found for the phosphinato P atom. Since all bond angle adjustment appears to be localized in the latter (the Co–P–C(51) angle, 113.3 (4)°, remains large), its interligand angle is considerably more acute than found in **6a** where the adjustment is spread between two P–OR bonds. Contrary to **6a**, a nearly planar geometry is found for the aminophosphine nitrogen atom. The projection of the H–N–C* angle orthogonal to the P–N plane gives a value of ca. 181°.

As with other related phosphonato and phosphinato complexes,[30,37,44] there is substantial double-bond character in the phosphoryl bond. Accordingly the P=O bond distance (149.9 (6) pm) is considerably shorter than the P-OMe bond distance (161.0 (6) pm). The presence of a strong P=O···H—N intramolecular hydrogen bond is confirmed by the short P(O)H–N distance (208 pm) which is considerably less than the sum of the van der Waals radii of N and H (260 pm).[46] Rogers' η method[47] was used to determine the absolute configuration of all three chiral atoms in **7a**. The aminophosphine, known to be *S* at carbon, provided an internal check of the assignments. Conventional *R*,*S* notation[49] with the ligand priority series I > η^5-Cp > P(O) > PN for cobalt fixes the absolute configuration of **7a** as S_{Co},R_P,S_C.[3,50]

Table VI. Atomic Coordinates (×10^4) and Isotropic Temperature Factors (pm^2 × 10^{-1}) for 7a

	x	*y*	*z*	U^a
I	994.8 (0.5)	2574.4 (0.4)	1905.1 (0.2)	58 (1)
Co	3185 (1)	3533 (1)	1926.6 (0.5)	38 (1)
P(1)	4393 (2)	2291 (1)	1623 (1)	41 (1)
P(2)	3655 (2)	3146 (1)	2864 (1)	43 (1)
C(11)	5443 (6)	3258 (4)	3012 (3)	37 (2)
C(12)	6229 (6)	2438 (5)	3044 (3)	46 (2)
C(13)	7602 (6)	2517 (6)	3101 (3)	60 (3)
C(14)	8188 (8)	3406 (6)	3101 (4)	60 (3)
C(15)	7438 (8)	4214 (6)	3070 (4)	54 (3)
C(16)	6055 (7)	4138 (5)	3037 (4)	50 (3)
C(21)	2911 (7)	3917 (5)	3428 (4)	45 (3)
C(22)	3551 (9)	4082 (6)	3971 (4)	63 (4)
C(23)	2962 (11)	4672 (7)	4396 (4)	79 (4)
C(24)	1729 (10)	5097 (6)	4275 (4)	75 (4)
C(25)	1099 (9)	4924 (7)	3745 (4)	77 (4)
C(26)	1692 (7)	4350 (5)	3330 (4)	55 (3)
C(31)	2689 (7)	1718 (5)	4118 (3)	48 (3)
C(32)	3965 (8)	1429 (6)	4252 (3)	56 (3)
C(33)	4426 (10)	1348 (7)	4832 (4)	84 (4)
C(34)	3583 (9)	1566 (4)	5286 (4)	90 (4)
C(35)	2272 (10)	1843 (8)	5181 (4)	101 (5)
C(36)	1824 (10)	1920 (6)	4599 (4)	75 (4)
c(41)	3408 (9)	5001 (5)	2101 (4)	62 (3)
C(42)	4446 (8)	4640 (5)	1749 (3)	58 (3)
C(43)	3898 (11)	4331 (5)	1214 (4)	68 (4)
C(44)	2514 (11)	4445 (6)	1251 (5)	80 (4)
C(45)	2235 (9)	4863 (5)	1803 (4)	76 (4)
C(51)	4069 (8)	1954 (5)	846 (3)	50 (3)
C(52)	4843 (9)	2352 (7)	378 (3)	76 (4)
C(53)	4613 (14)	2025 (9)	–210 (5)	103 (6)
C(54)	3701 (16)	1355 (9)	–333 (5)	115 (7)
C(55)	2984 (12)	941 (8)	113 (5)	95 (5)
C(56)	3154 (9)	1259 (6)	707 (4)	75 (4)
N	3230 (5)	2032 (4)	3059 (3)	39 (2)
C(1)	2171 (7)	1766 (5)	3483 (3)	43 (3)
C(2)	1583 (8)	809 (6)	3306 (4)	67 (4)
O(1)	4334 (5)	1399 (3)	1996 (2)	49 (2)
O(2)	5882 (5)	2728 (3)	1586 (2)	51 (2)
C(O2)	6977 (9)	2070 (7)	1510 (4)	79 (4)
H(N)	3724	1517	2878	49

[a] Equivalent isotropic *U* defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

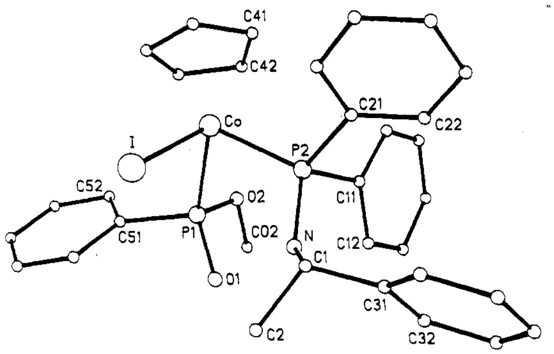


Figure 8. Molecular geometry and absolute configuration of **7a**.

Circular dichroism (CD) spectra (cf. Figure 9a,b) in combination with epimerization studies allowed determination of the absolute configuration of all diastereomers

Table VII. Summary of Crystallographic Data for 6a and 7a

	6a	7a
formula	$C_{27}H_{31}CoINO_3P_2$	$C_{32}H_{33}CoINO_2P_2$
cryst habit	black hexagonal plate	dark brown prism
cryst size, mm	0.4 × 0.4 × 0.15	0.4 × 0.23 × 0.1
cell const (Å)		
a	9.470 (2)	9.995 (2)
b	15.136 (3)	13.934 (5)
c	19.562 (4)	22.422 (5)
space group	$P2_12_12_1$	$P2_12_12_1$
U (Å^3)	2804	3123
Z	4	4
D_{calcd} (g cm^{-3})	1.58	1.51
μ (mm^{-1})	1.8	1.7
absn correctn (transmissns)	ψ-scans (0.71–0.92)	ψ-scans (0.72–0.82)
$2\theta_{max}$ (deg)	55	50
octants measd	hkl and $\bar{k}\bar{k}\bar{l}$	hkl and $\bar{h}\bar{k}\bar{l}$
reflctns measd	6287	6066
unique reflectns	5652	5376
R_{int}	0.016	0.023
obsd reflctns ($F > 4\sigma(F)$	4721	3749
R	0.041	0.058
R'	0.036	0.044
g	0.0002	0.00015
no. of parameters	325	358
max $\Delta\rho$ (e Å^{-3})	0.7 (near I)	0.85 (near I)
η	+1.07 (4)	+1.05 (6)

7a–d. Since chiroptical properties are generally dominated by the transition metal,[3] comparison of the CD curves of $(+)_{436}$-**7a** and $(+)_{436}$-**7c** shows that they have identical configuration, S, at cobalt. The configuration at the aminophosphine carbon is S; hence their diastereomeric relationship requires that they the epimeric at phosphorus. Thus the absolute configuration of **7c** is S_{Co},S_P,S_C.[50] Similarly, CD spectra (cf. Figure 9a,b) show that the absolute configuration at Co in $(-)_{436}$-**7b** and $(-)_{436}$-**7d** is identical but opposite that of **7a** and **7c**. The assignment of absolute configuration at the phosphorus atom in **7b,d** relies on the observation that isomerization in solution *specifically*[56] interconverts **7a–7d** and **7b–7c**. If the isomerization is a simple Co epimerization as the CD evidence suggests, the above arguments require that the pairs **7a,d** and **7b,c** have identical configuration at phosphorus. Hence $(-)_{436}$-**7b** is assigned the absolute configuration R_{Co},S_P,S_C[50] while $(-)_{436}$-**7d** is R_{Co},R_P,S_C.[50]

Solid-State Conformation of 7a. Figure 10 shows ORTEP drawings of the Newman projections for **7a** along the P(O)–Co, PN–Co, and P–N bonds. Only very minor conformational changes appear to result on replacement of a methoxy by a phenyl substituent. As found for **6a**, the conformation about the P(O)–Co and PN–Co bonds is staggered with the η^5-Cp ring trans to the phosphoryl oxygen and nitrogen, respectively (Figure 10a,b). The unusual trans N–η^5-Cp conformation[51,52] finds its origin in the strong intramolecular hydrogen bonding[45] which establishes the quasi-chair shown in the projection of Figure 10c. Although the nitrogen atom is considerably more planar in **7a** compared to **6a**, η^5-Cp and I remain pseudoequatorial and -axial, respectively, allowing the P(O)*Ph* and the less sterically demanding P(O)*OMe* to occupy equatorial and axial positions, respectively.

Solution Conformation of 7a,b. Proton nuclear Overhauser difference (NOED) spectra (cf. Figure 11) of S_{Co},R_P,S_C-**7a** are in accord with the retention of an intramolecular hydrogen-bonded quasi-chair conformation in solution. Reference to Figure 12 shows that in conformation C, η^5-Cp is pseudoequatorial and the gauche to both diastereotopic aminophosphine phenyl groups as well as the pseudoequatorial P(O)*Ph* and pseudoaxial OMe. Inspection of Figure 11b shows that irradiation of the η^5-Cp resonance gives strong Overhauser enhancements for the ortho protons of all three phenyl groups as well as the methoxy group. Proton NOED spectra of R_{Co},S_P,S_C-**7b**, which has the opposite configuration at cobalt and phosphorus, show similar effects and are fully in accord with preferential population of the same relative conformation D (Figure 12) which retains an equatorial η^5-Cp ring. It is likely that the origin of the conformational bias is the stabilizing interaction[12,39] between η^5-Cp and *both* face-exposed gauche aminophosphine phenyl groups which is possible only when η^5-Cp is equatorial (Figure 12, conformation C for **7a** and conformation D for **7b**).

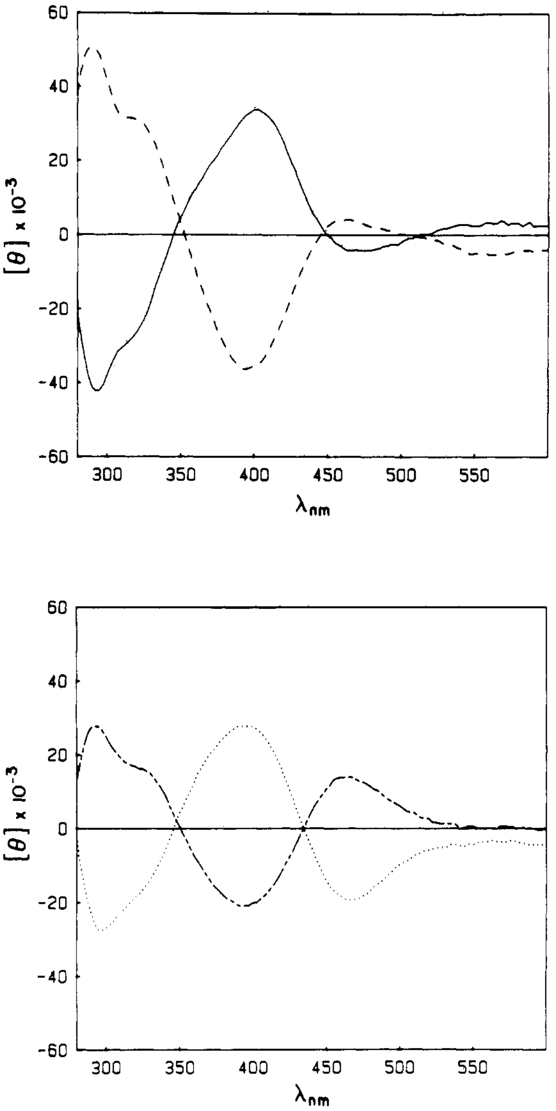


Figure 9. Top: circular dichroism spectra for **7a** (———) and **7a** (- - -) in toluene solution. Bottom: circular dichroism spectra for **7c** (···) and **7d** (———) in toluene solution.

Assumption of a productlike transition state for dealkylation of prochiral phosphorus leading to **7** provides a rationale for the significant degree of optical induction found on formation of the chiral P center. If an S cobalt forms on initial substitution the kinetic product in methylene chloride is S_{Co},R_P,S_C-**7a** (% ee = 80.4). Formation of R cobalt results in R_{Co},S_P,S_C-**7b** (% ee = 77.8) as the major product. In the case of the minor products, **7c** and

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[56] Proton NMR spectra or thin-layer chromatography of equilibrated toluene or methylene chloride solutions of **7a** or **7d** showed specific formation of **7d** and **7a**, respectively. Similar results were obtained with **7b,c**.

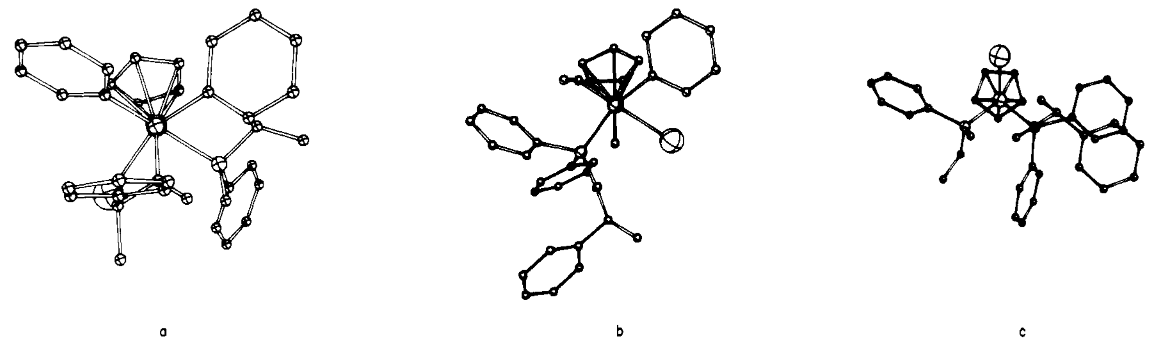

Figure 10. ORTEP drawings of Newman projections for **7a**.

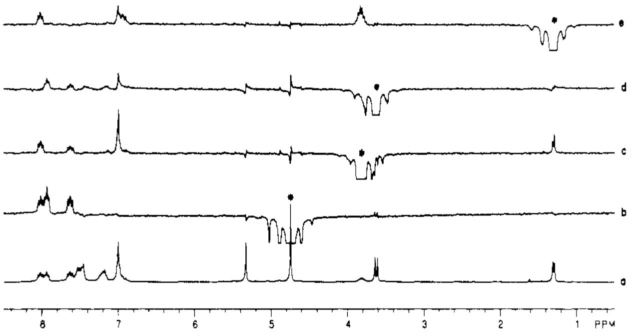

Figure 11. Proton NOED spectra for **7a**: (a) reference spectrum; (b–e) difference spectra (64X) for irradiation at the indicated asterisk (*) frequency; (b) η^5-Cp; (c) C*H*Me; (d) OMe; (e) CH*Me*.

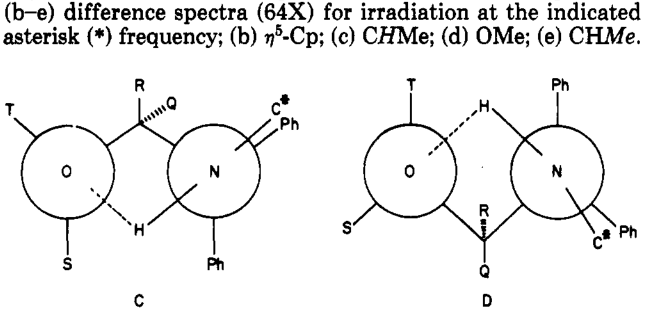

Figure 12. Solution conformation for **7**: **7a**, Q = η^5-Cp, R = I, S = OMe, T = Ph; **7b**, Q = I, R = η^5-Cp, S = Ph, T = OMe; **7c**, Q = η^5-Cp, R = I, S = Ph, T = OMe; **7d**, Q = I, R = η^5-Cp, S = OMe, T = Ph.

7d, the conformer with equatorial η^5-Cp requires a potentially destabilizing 1,3 diaxial phenyl interaction as in C and D, respectively (cf. Figure 12); thus transition states leading to **7c,d** are higher energy. Quite clearly, intramolecular hydrogen bonding appears to play a central role in determining the extent of optical induction observed in the dealkylation at prochiral phosphorus.

Experimental Section

Reagents and Methods. All manipulations were performed under a nitrogen atmosphere by using standard Schlenk techniques. Nitrogen gas was purified by passing through a series of columns containing concentrated sulfuric acid, granular phosphorus pentoxide, and potassium hydroxide. Toluene, benzene, and ether were distilled from blue solutions of sodium benzophenone ketyl. Methylene chloride was freshly distilled from P_4O_{10}. Acetone was distilled from activated 3A molecular sieves. NMR spectra were recorded on a Bruker WM 250 or a General Electric 300-NB spectrometer. Solution IR spectra were recorded in 0.5-mm path length KRS-5 cells on a Perkin-Elmer Model 283 spectrophotometer. Optical rotation measurements were determined in toluene (ca. 1 mg/mL) in a 1-cm path length cell by 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. Mass spectra (70-eV electron impact and field desorption) were recorded on a Finningan MAT 311 instrument. Melting points were determined in sealed capillaries by using a Büchi-SMP-20 apparatus and are uncorrected. Elemental analyses were performed by the Central Microanalytical Laboratory, University Regensburg. The compounds η^5-$CpCoI_2(CO)$[57] (*S*)-(−)-diphenyl((1-phenylethyl)amino)phosphine,[58] and methyl phenylphosphinate[59] were prepared by using the established procedures. Sodium methyl phenylphosphinate was prepared by using a modification of Kosolapoff's method.[60] Commercial samples of trimethyl phosphite and dichlorophenylphosphine were distilled before use. Dimethyl phenylphosphonite and 1,9-bis(diethylamino)naphthalene (Proton Sponge, Aldrich) were used as received.

Proton NOED spectra were determined under steady-state conditions on a GE 300-NB instrument using a set of 16K interleaved experiments of eight transients cycled 12 to 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 24-s delay preceded each frequency change. A set of four "dummy" 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 zero-filled 32K data tables which had been digitally filtered with a 1–2-Hz exponential line broadening function.

Crystal Structure Determinations. Data were collected on a Stoe-Siemens four-circle diffractometer at 293 K in profile fitting mode[61] using monochromated Mo Kα radiation (λ = 0.71069 Å). Cell constants were refined from 2θ values of selected strong reflections in the range 20–23°. The structures were solved by the heavy-atom method and refined anisotropically on $|F|$. Hydrogen atoms were included in the refinement by using a riding model. Weighting schemes were of the form $w^{-1} = \sigma^2(F) + gF^2$. Absolute configurations were determined by Rogers' η method.[47] The program system was SHELXTL (written by Prof. G. M. Sheldrick), which incorporates atomic scattering factors from ref 62. Further details are given in Table VII.

Preparation of (*S*)-η^5-$CpCoI_2(PPh_2N(H)C^*H(Me)Ph)$ (4). A solution of (*S*)-(−)-diphenyl((1-phenylethyl)amino)phosphine (3.01 g, 9.87 mmol) in 50 mL of benzene was added dropwise to a stirred solution of η^5-$CpCoI_2(CO)$ (3.64 g, 8.97 mmol) in 50 mL of benzene. Gas evolution begins immediately, and the color changes from purple to black. After the mixture was stirred for 1 h at room temperature, the volatiles were removed at aspirator pressure and the resulting sticky, black residue was washed with several portions of hexane to remove unreacted aminophosphine ligand. The crude product was collected as a black powder and purified by chromatography on deactivated (10% water) Kieselgel. Toluene elution moved a purple zone which was collected and crystallized from methylene chloride/hexane to give 4.17 g (68%) of the title compound as long black needles: mp 168–169 °C; FDMS, *m/e* 683 ($M^{\bullet+}$). Anal. Calcd. for $C_{25}H_{25}CoI_2NP$: C, 43.94;

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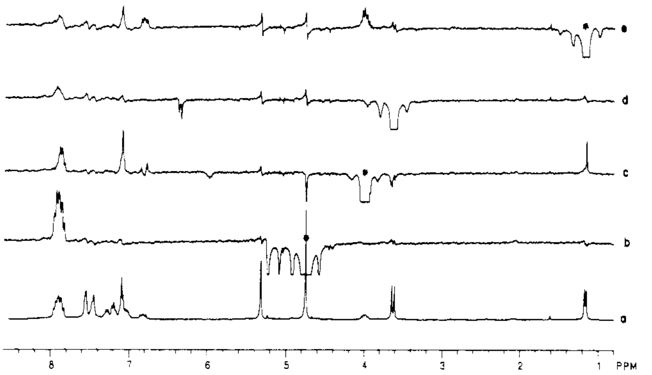

Figure 13. Proton NOED spectra for **7b**: (a) reference spectrum; (b–e) difference spectra (64X) for irradiation at the indicated asterisk (*) frequency; (b) η^5-Cp; (c) C*H*Me; (d) OMe; (e) CH*Me*.

H, 3.66. Found: C, 43.79; H, 3.71.

Preparation of (R,S_{Co},S_C)-η^5-CpCoI(PPh$_2$N(H)C*H(Me)Ph)(P(O)(OMe)$_2$) (6). A solution of 95 mg (91 μL, 0.77 mmol) of trimethylphosphite in 10 mL of benzene was added dropwise to a solution of 500 mg (0.73 mmol) of (S)-η^5-CpCoI$_2$(PPh$_2$N(H)C*H(Me)Ph) (4) in 10 mL of the same solvent. The deep purple solution rapidly turns brown and then slowly turns green-yellow. After the mixture was stirred at room temperature for an additional 1 h, the volatiles were removed at reduced pressure (0.1 mmHg). The dark green, sticky residue was washed with several portions of hexane, taken up in 1:1 methylene chloride/acetone, and filtered through a small plug of silica gel. The diastereomers were separated by chromatography through two Lobar (Merck, size B, LiChroprep 40–63 μm) columns in series. Elution with 12:1 methylene chloride/acetone followed by crystallization from toluene/hexane gave 203 mg of the less soluble, higher R_f diastereomer (S_{Co},S_C)-η^5-CpCoI(PPh$_2$N(H)C*H(Me)Ph)(P(O)(OMe)$_2$) (**6a**) (mp dec > 188 °C; $[\alpha]_{436}$ +5760° (optical purity 82.8%)) and 220 mg of the more soluble, lower R_f diastereomer (R_{Co},S_C)-η^5-CpCoI(PPh$_2$N(H)C*H(Me)Ph)(P(O)(OMe)$_2$) (**6b**) (mp dec > 180 °C; $[\alpha]_{436}$ −5090° (optical purity 85.6 %)). Anal. Calcd for $C_{27}H_{31}CoINO_3P_2$ (**6a**); C, 48.74; H, 4.70; N, 2.11. Found: C, 48.99; H, 4.63; N, 2.13. **6a**: FDMS, *m/e* 665 ($M^{\bullet+}$), 556 (M^+ − P(O)(OMe)$_2$), 429 (556 − I). **6b**: FDMS, *m/e* 665 ($M^{\bullet+}$).

Preparation. (R,S_{Co},R,S_P,S_C)-η^5-CpCoI(PPh$_2$N(H)C*H(Me)Ph)(PhP(O)(OMe)) (7). Method a. A solution of 131 mg (121 μL, 0.769 mmol) of PPh(OMe)$_2$ in 10 mL of benzene was slowly added to a stirred solution of 500 mg (0.732 mmol) of (S)-η^5-CpCoI$_2$(PPh$_2$N(H)C*H(Me)Ph) (4) in 10 mL of the same solvent. The deep purple solution immediately turned brown followed by a slow conversion to dark green. After the mixture was stirred for 1 h at room temperature, the volatiles were removed at reduced pressure (0.1 mmHg). The resulting dark green gum was washed with hexane, taken up in a small volume of 1:1 methylene chloride/acetone, and filtered through a short plug of silica gel. Removal of solvent gave the title compound as a dark green solid composed of a mixture of diastereomers. Separation of all four diastereomers was accomplished by chromatography on three Lobar (Merck, size B, LiChroprep 40–63 μm) columns connected in series. Elution with 12:1 methylene chloride/acetone moved two pairs of widely separated green zones. The first pair of faster moving zones was eluted with 12:1 methylene chloride/acetone to give **7a** (226 mg) and **7b** (190 mg). The second pair of slower moving zones was eluted with 4:1 methylene chloride/acetone to give **7c** (29 mg) and **7d** (38 mg). Several recrystallizations from toluene/hexane gave essentially diastereomerically pure products. (S_{Co},R_P,S_C)-η^5-CpCoI(PPh$_2$N(H)C*H(Me)Ph)(PhP(O)(OMe)) (**7a**): $[\alpha]_{436}$ +2906°; mp 168 °C; FDMS, *m/e* 711 ($M^{\bullet+}$). Anal. Calcd for $C_{32}H_{33}CoINO_2P_2$: C, 54.06; H, 4.68; N, 1.97. Found: C, 54.16; H, 4.78; N, 1.92. (R_{Co},S_P,S_C)-η^5-CpCoI(PPh$_2$N(H)C*H(Me)Ph)(PhP(O)(OMe)) (**7b**): $[\alpha]_{436}$ −3100°; mp 174 °C; FDMS, *m/e* 711 ($M^{\bullet+}$). Anal. Calcd for $C_{32}H_{33}CoINO_2P_2$: C, 54.06; H, 4.68; N, 1.97. Found: C, 54.13; H, 4.75; N, 1.84. (S_{Co},S_P,S_C)-η^5-CpCoI(PPh$_2$N(H)C*H(Me)Ph)(PhP(O)(OMe)) (**7c**): $[\alpha]_{436}$ +4489°; FDMS *m/e* 711 ($M^{\bullet+}$). ($R_{Co}$$R_P$$S_C$)-CpCoI((PPh$_2$N(H)C*H(Me)Ph)(PhP(O)(OMe)) (**7d**): $[\alpha]_{436}$ −3408°; FDMS, *m/e* 711 ($M^{\bullet+}$. Continued elution with 4:1 methylene chloride/acetone separated small amount of several minor products, one of which was tentatively identified on the basis of NMR evidence as a diastereomeric η^5-CpCoI(PPh(OMe)$_2$)(PhP(O)(OMe)) formed by substitution of the aminophosphine ligand. Alternatively, the least soluble diastereomerisomer **7b** can be fractionally crystallized by cooling an acetone solution of the crude product. The remaining three diastereomers separated chromatographically following the method described above.

Method b. A deep purple solution of 200 mg (0.293 mmol) of (S)-η^5-CpCoI$_2$(PPh$_2$N(H)C*H(Me)Ph) (4), 78 mg (0.29 mmol) of 1,9-bis(diethylamino)naphthalene (Proton Sponge), and 45 mg (0.29 mmol) of methyl phenylphosphinate was refluxed in benzene under N_2. After 12 h the resulting green solution was filtered through Celite. Volatiles were removed at reduced pressure (0.1 mmHg) to leave a sticky green solid which was dissolved in methylene chloride and purified by filtration through a short plug of silica. NMR analysis showed a 82.4% conversion to the methyl phenylphosphinato complex 7 with an isomer distribution of **7a**:**7b**:**7c**:**7d** = 5.6:5.7:1:1.6.

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Registry No. 4, 113109-08-3; **6a**, 113089-43-3; **6b**, 113158-94-4; **7a**, 113089-44-4; **7b**, 113158-95-5; **7c**, 113158-96-6; **7d**, 113158-97-7; η^5-CpCoI$_2$(CO), 12012-77-0; (S)-(−)-Ph$_2$PNHCHMePh, 71554-93-3; P(OMe)$_3$, 121-45-9; PPh(OMe)$_2$, 2946-61-4; P(O)Ph(OMe), 7162-15-4.

Supplementary Material Available: Tables of bond distances and angles, anisotropic temperature factors, and atom coordinates for **6a** and **7a** (10 pages); listings of structure factors for **6a** and **7a** (66 pages). Ordering information is given on any current masthead page.