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Preparation, crystal structure, absolute configuration, and conformational analysis of $(-)_{436}$-(*S*)-(−)-diphenyl-1-phenylethylaminophosphine(η^5-pentamethylcyclopentadienyl)-(dimethylphosphonato)cobalt(III)

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Abstract

Reaction of $Cp^*CoI_2(P(OMe)_3)$ (**8**) with the chiral aminophosphine (*S*)-(−)-diphenyl-1-phenylethylaminophosphine affords the diastereomeric phosphonate complexes $(R,S)_{Co},S_C$-$Cp^*CoI(P(O)(OMe)_2)(PPh_2NHC^*H(Me)Ph)$ (**10a,10b**) via Arbuzov dealkylation. **10a,10b** are separable and configurationally stable in solution for extended periods.The structure and absolute configuration of the lower R_f diastereomer $(-)_{436}$-**10b** were determined via single-crystal X-ray diffraction. It crystallizes as a toluene solvate in space group $P2_1$ with *a* 13.194(6), *b* 9.062(4), *c* 17.023(5) Å, β 108.78(3)°, $Z = 2$, and was refined to $R = 0.067$ for 6318 reflections. Spectroscopic and structural evidence demonstrate a strong 1,6 intramolecular NH · · · O=P hydrogen bond between the aminophosphine NH and the basic phosphoryl oxygen, which establishes a quasi-boat conformation. Proton nuclear Overhauser difference spectra show that the conformation in solution is the same as that observed in the solid state.

Introduction

Previously [1] we reported that initial substitution of prochiral iodide in the pseudo-octahedral aminophosphine Cp cobalt complex **1** was followed by an Arbuzov-like dealkylation [2,3,4] which afforded the chiral phosphonate complex **3** (R′ = OR, Ar). Intramolecular hydrogen P=O · · · HNP bonding between the basic phosphoryl oxygen and the aminophosphine NH was proposed to play a dominant

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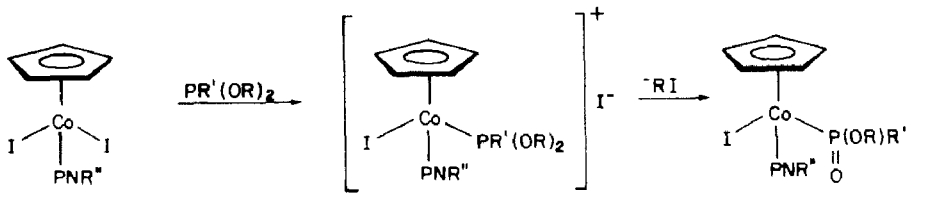

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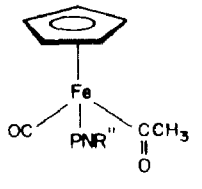

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R = CH_3 ; R' = OCH_3 , Ph
PNR" = $PPH_2CR''(Me)Ph$;
R" = H , CH_3 , C_2H_5

role in the observed chiral induction at prochiral α-phosphorus. The same hydrogen bonding interaction can be projected to "anchor" the aminophosphine and thereby impede its dissociation. Since the dominant transition metal epimerization mechanism for complexes of this type emergent from Brunner's work is dissociative [5,6], intramolecular hydrogen bonding may also have important implications relating to the stability observed for the chiral cobalt atom in the complexes **3** and to the stereochemical integrity of chiral metal atoms in general. For example Brunner has reported [6] that the configurational stability at Fe in the chiral complexes **4** increases as the aminophosphine changes from 3° to 2°. The observed trend can be interpreted [6] in terms of a sterically assisted, dissociative Fe-epimerization which rationally correlates with steric requirements of the aminophosphine ligand. However the PNH · · · O=C intramolecular hydrogen bond found [7] for **4** (R = H) in the solid state suggests that other factors may also contribute to the increased configurational stability of the 2° aminophosphine derivative.

In view of these ambiguities, a more comprehensive determination of the role played by intramolecular hydrogen bonding in determining the stereochemical lifetimes of chiral transition metal atoms in "pianostool" complexes seems in order. In particular we wished to examine the generality of the proposed influence of intramolecular hydrogen bonding on configurational stability and to seek additional examples to further test the hypothesis. This work reports a comparison of our earlier results [1] with the structurally analogous pentamethylcyclopentadiene (Cp^*) derivative. Our choice of structural perturbation by the exchange of Cp^* for Cp rests on its demonstrated ability to act as a stronger σ-donor [8,9] and its increased steric demands [10,11] which are intuitively expected to facilitate dissociative reactions.

Experimental

Reagents and methods

All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques. Nitrogen gas was purified by passing through a series of

columns containing DEOX (Alpha) catalyst heated to 120 °C, granular phosphorus pentoxide, and activated molecular sieves. Toluene, benzene, and hexane 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. NMR spectra were recorded on a General Electric 300-NB spectrometer. Chemical shifts are reported in ppm relative to internal TMS; coupling constants in Hz. Solution IR spectra were recorded in 0.1 mm pathlength KBr cells on a Perkin–Elmer Model 283 spectrophotometer. Optical rotation measurements were determined in toluene (ca. 1 mg/ml) in a 1 cm pathlength cell using a Perkin–Elmer Model 241 polarimeter. CD spectra were determined in toluene (ca. 1 mg/ml) on a Jasco J40A apparatus using a 0.1 cm pathlength cell. Mass spectra (FAB/glycerol/*p*-toluenesulfonic acid) were recorded on a VG Instruments 7070HS instrument using a VG 2035 data system. Melting points were determined in sealed capillaries and are uncorrected. Elemental analyses were performed by Guelph Chemical Labs. The η^5-pentamethylcyclopentadienyl complexes η^5-Cp*$Co(CO)_2$, η^5-Cp*$CoI_2(CO)$, and $[\eta^5$-Cp*$CoI_2]_2$ were prepared according to the method of Frith and Spencer [12]. (*S*)-(−)-diphenyl-1-phenylethylaminophosphine was prepared using the established procedure [13]. Trimethyl phosphite was purchased from Strem and was distilled from Na before use. (*S*)-(−)-α-methylbenzylamine was purchased from Aldrich and used as received.

Proton nuclear Overhauser enhancement difference (NOED) spectra were determined under steady state conditions on a GE 300-NB instrument using a set of 16 K interleaved experiments of 8 transients cycled 12 to 16 times through the list of decoupling frequencies. The temperature was thermostatted at 25 ± 0.1 °C. 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 "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 32 K data tables that had been digitally filtered with a 1–2 Hz exponential line broadening function.

Crystal structure determination

Data collection and reduction. A brownish-black prism 0.4 × 0.25 × 0.15 mm was mounted in a glass capillary. 10503 profile-fitted [14] intensities were registered on a Stoe–Siemens four-circle diffractometer using monochromated Mo-K_α radiation ($2\theta_{max}$ 55°, hemisphere with positive *l*). An empirical absorption correction based on ψ-scans gave transmission factors 0.63–0.74. Cell constants were refined from 2θ values of 48 reflections in the range 20–23°. Merging equivalents gave 8891 unique reflections ($R_{int} = 0.047$), of which 6318 with $F > 4\sigma(F)$ were used for all calculations (program system SHELX, modified by its author Prof. G.M. Sheldrick).

Structure solution and refinement. Heavy atom method, followed by full-matrix anisotropic least-squares refinement on *F*. H atoms were included using a riding model. A molecule of toluene of crystallisation was identified and refined isotropically with idealised ring geometry. The absolute configuration was determined with an η refinement [15]; $\eta = -1.01(6)$, whereupon the model was inverted for final cycles. Final $R = 0.067$, $R_w = 0.060$.The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0006F^2$. 376 parameters; *S* 1.3; max Δ/σ 0.002; max. $\Delta\rho$ 1.5 e Å^{-3} near the I

Table 1

Selected bond distances and bond angles for $(-)_{436}$-**10b**

Bond	Distance (Å)	Bond	Angle (deg)
I–Co	2.585(1)	I–Co–P(2)	94.5(1)
Co–P(1)	2.197(2)	I–Co–P(1)	89.4(1)
Co–P(2)	2.237(3)	P(1)–Co–P(2)	90.6(1)
P(1)–O(1)	1.483(7)	Co–P(1)–O(1)	120.8(3)
P(1)–O(2)	1.620(7)	O(1)–P(1)–O(2)	108.8(4)
P(1)–O(3)	1.612(6)	Co–P(1)–O(2)	110.3(3)
		Co–P(1)–O(3)	105.3(2)
N–P(2)	1.660(7)	O(2)–P(1)–O(3)	99.5(4)
NH · · · O(1)	2.151	O(1)–P(1)–O(3)	109.9(4)

atom. Further details are given in Table 2. Selected bond distances and bond angles are given in Table 1, and atomic coordinates and isotropic temperature factors are reported in Table 3. Complete crystallographic details have been deposited and are available on request [16*].

*Preparation of $Cp^*CoI_2(P(OMe)_3)$ (**8**)*

Under a dry, dinitrogen atmosphere a three-neck flask equipped with magnetic stirrer, dropping funnel, condensor, and gas inlet was charged with 0.2757 g (0.5792 mmol) of $Cp^*CoI_2(CO)$ in 20 ml of dry benzene. One equivalent of $P(OMe)_3$ (68 μl) in 25 ml of degassed benzene was added slowly at room temperature. Carbon monoxide evolution occurred almost immediately. After addition was complete and one equivalent of CO gas had been collected the reaction mixture was allowed to stir for 0.5 h. Removal of volatiles gave the crude product as a purple-black solid. Chromatography on a 30×1 cm column using Baker 60–200 mesh silica gel with 25/1 dichloromethane/acetone elution followed by crystallization from methylene chloride/hexane at $-20\,^\circ$C afforded the product as purple-black crystals (63%), m.p. 158.5–160.3 $\pm$ 2 °C. The product is air stable indefinitely in the solid state and for extended periods in solution. Anal. Found: C, 27.48; H, 4.17. $C_{13}H_{24}CoI_2PO_3$ calcd.: C, 27.30; H, 4.23%. ^{1}H NMR ($CDCl_3$) 3.84 (d, J 9.8 Hz, 9H, OCH_3), 1.96 (d, J 2.6 Hz, 15H, $C_5(CH_3)_5$).

*Preparation of $(R,S)_{Co},S_C$-$Cp^*CoI(P(O)(OMe)_2)(PPh_2NHC^*H(Me)Ph)$ (**10a,10b**)*

A three neck flask fitted with dropping funnel, stirrer, and gas inlet was charged with a solution of 1.5341 g (2.68 mmole) $Cp^*CoI_2(P(OMe)_3)$ in 25 ml dry benzene. Excess (*S*)-(−)-diphenyl-1-phenylethylaminophosphine (3.02 g, 9.89 mmol) in 10 ml of benzene solution was added quickly at room temperature under an atmosphere of dry dinitrogen and the solution was then warmed to 55 °C. After 13.5 h, the solvent was removed at reduced pressure leaving a dark green oil. Excess (*S*)-(−)-diphenyl-1-phenylethylaminophosphine was removed by chromatography in 1/2/1 hexane/methylene chloride/acetone on a 5×50 cm column of 60–200 mesh silica gel. Separation of diastereomers was accomplished by thin layer chro-

* Reference numbers with asterisks indicate notes in the list of references.

Table 2

Summary of crystallographic data for $(-)_{436}$-**10b**

Formula	$C_{32}H_{41}CoINO_3P_2 \cdot C_7H_8$
Crystal habit	dark brown prism
Crystal size	$0.4 \times 0.25 \times 0.15$ mm
$F(000)$	848
s	1.3
M	827.6
Cell constants	
a	13.1934(6) Å
b	9.062(4) Å
c	17.023(5) Å
α	90°
β	108.78(3)°
γ	90°
space group	$P2_1$
U	1927 Å^3
Z	2
D_x (g cm^{-3})	1.43
μ	1.4 mm^{-1}
λ(Mo-K_α)	0.71069 Å
Absorption correction (transmissions)	ψ-scans (0.63–0.74)
$2\theta_{max}$ (deg)	55
Hemisphere measured	$\pm h \pm k + l$
Reflections measured	10,503
Unique reflections	8,891
R_{int}	0.047
Observed reflections $F > 4\sigma(F)$	6318
R	0.067
R'	0.060
g	0.0006
No. of parameters	376
Max. $\Delta\rho$	1.5 (near I) e Å^{-3}
Max. Δ/σ	0.002
η	−1.01(6)

matography on a preparative 2 mm thick silica gel plate. Elution with 4/1 hexane/ethyl acetate moved the Co epimeric products as two closely spaced green zones corresponding to **10a,10b**.

The lower R_f band, **10b**, was crystallized by slow cooling of a toluene/acetone solution to give large brown-black prisms of diastereomerically pure product $(-)_{436}$-**10b** (m.p. 170.5–171.6°C); $[\alpha]_{365} = +5830$, $[\alpha]_{436} = -3656$; Anal. Found: C, 56.68; H, 5.88; N, 1.64. $C_{32}H_{41}CoIP_2NO_3 \cdot C_7H_8$ calcd.: C, 56.60; H, 5.97; N, 1.69%. Mass spectrum (FAB/glycerol/PTSA): m/e, (rel. intensity, assignment). 738 (5.51, $MH^+ + 2H$), 627 (3.50, $MH^+ - P(O)(OMe)_2$), 626 (11.4, $MH^+ - P(OH)(OMe)_2$), 500 (11.03, 627 − I), 499 (33.63, 626 − I), 491 (13.78, 626 − Cp*), 432 (14.22, MH^+ + H-(*S*)-(−)-diphenyl-1-phenylethylaminophosphine), 431 (92.29, MH^+ − (*S*)-(−)-diphenyl-1-phenylethylaminophosphine), 394 (12.68, not assigned), 365 (37.93, 500 − Cp*), 322 (12.13, 432 − $P(OH)(OCH_3)_2$), 321 (77.24, 431 − $P(OH)(OCH_3)_2$), 307 (14.88, not assigned), 306 (62.84, (*S*)-(−)-diphenyl-1-phenylethylaminophosphine$^+$), 304 (12.68, 431 − 1), 303 (10.25, 431 − HI); ^{1}H NMR

Table 3

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters for $(-)_{436}$-**10b**

	x	*y*	*z*	*U*(eq) [a]
Co	6008(1)	5338(1)	8342.3(6)	27(1)
I	6724.7(5)	8000	8666.2(4)	44(1)
P(1)	4861(2)	6122(2)	7171(1)	33(1)
P(2)	7168(2)	4718(2)	7686(1)	31(1)
O(1)	5234(5)	6922(7)	6554(4)	48(3)
O(2)	3919(6)	7071(8)	7350(5)	51(3)
C(02)	3816(11)	8598(12)	7166(10)	75(6)
I(3)	4186(5)	4684(7)	6748(4)	44(2)
C(03)	3389(10)	4802(16)	5970(7)	72(5)
C(11)	8536(7)	4313(10)	8348(6)	43(3)
C(12)	9182(9)	3325(13)	8098(7)	67(5)
C(13)	10251(10)	3150(24)	8613(9)	103(7)
C(14)	10649(11)	3883(18)	9324(10)	94(7)
C(15)	9996(10)	4881(15)	9571(8)	77(5)
C(16)	8952(8)	5092(12)	9072(7)	57(4)
C(21)	6756(7)	3126(11)	7005(5)	35(3)
C(22)	6977(11)	1659(11)	7275(7)	56(5)
C(23)	6493(12)	501(13)	6730(8)	76(6)
C(24)	5884(11)	795(12)	5964(9)	70(6)
C(25)	5657(10)	2211(12)	5646(8)	67(5)
C(26)	6100(8)	3363(10)	6185(6)	50(4)
N	7356(6)	6077(7)	7094(4)	31(2)
C(1)	8090(7)	6006(10)	6617(6)	41(4)
C(2)	7578(10)	6835(14)	5795(7)	61(5)
C(31)	9200(9)	6628(10)	7089(6)	43(4)
C(32)	9360(9)	7591(11)	7731(7)	62(5)
C(33)	10394(10)	8057(23)	8133(8)	92(6)
C(34)	11247(10)	7655(17)	7867(9)	79(6)
C(35)	11059(11)	6728(17)	7263(10)	82(7)
C(36)	10039(9)	6190(15)	6831(7)	64(5)
C(41)	5321(7)	5457(10)	9292(6)	40(3)
C(42)	4718(8)	4474(10)	8695(6)	40(3)
C(43)	5397(7)	3329(8)	8597(5)	36(3)
C(44)	6430(8)	3551(9)	9223(5)	37(3)
C(45)	6390(8)	4878(10)	9642(5)	40(3)
C(46)	4894(11)	6733(13)	9638(7)	66(5)
C(47)	3510(8)	4473(13)	8310(7)	60(5)
C(48)	5021(9)	1990(10)	8075(7)	51(4)
C(49)	7318(9)	2449(10)	9479(7)	52(4)
C(50)	7233(9)	5469(12)	10391(6)	58(4)
C(1S)	10569(9)	1915(18)	6186(9)	172(10)
C(2S)	10421	2919	5538	115(5)
C(3S)	9389	3273	5030	194(10)
C(4S)	8505	2621	5171	211(12)
C(5S)	8653	1617	5820	111(6)
C(6S)	9685	1264	6327	122(6)
C(7S)	11567(27)	1637(43)	6677(20)	232(14)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

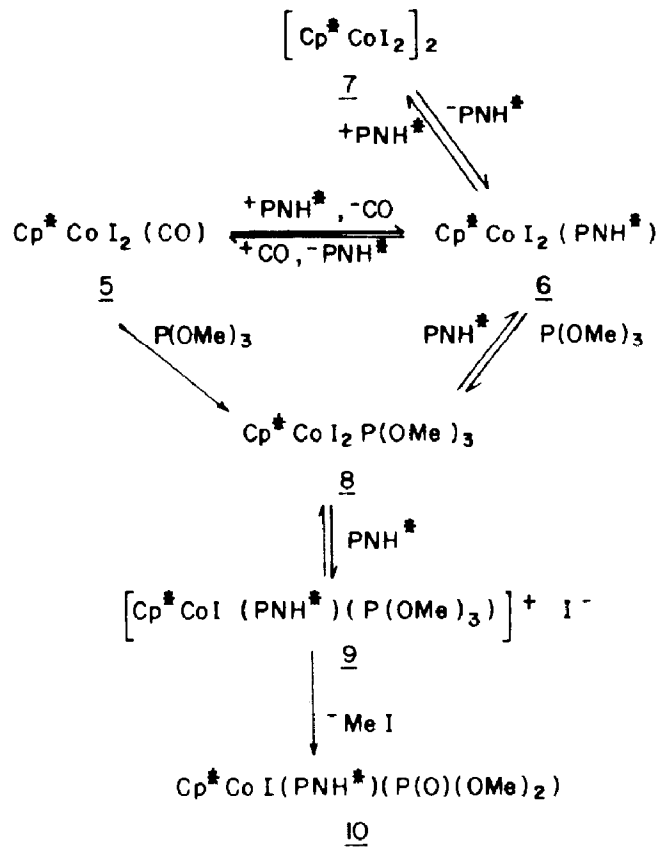
(CD_2Cl_2): δ (multiplicity, coupling constant in Hz, rel. integration, assignment): 8.02 (m, 2H, *o*-PC_6H_5), 7.80 (m, 2H, *o*-PC_6H_5), 7.47 (m, 2H, *m*-PC_6H_5), 7.44 (m, 1H, *p*-PC_6H_5), 7.14 (m, 1H, *p*-PC_6H_5), 7.08 (m, 2H, *m*-PC_6H_5), 6.86 (m, 5H,

$C^{\star}C_6H_5$), 6.47 (dd, ^3J(PH) 15.4, ^3J(HH) = 6.3, 1H, NH), 3.92 (m, ^3J(PH) 10.1, ^3J(HH) 6.7, ^3J(HH) 6.1, 1H, C*H), 3.70 (d, ^3J(PH) 11.0, 3H, OCH_3), 3.79 (d, 3H, ^3J(PH) 10.2, OCH_3), 1.40 (t, ^4J(PH) ≤ 1, 15H, $C_5(CH_3)_5$), 1.30 (d, ^3J(HH) 6.7, 3H, C*H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (multiplicity, coupling constant in Hz, assignment): 147.41 (s, –, *i*-CC_6H_5), 136.19 (d, J(PC) 10.7, *o*- or *m*-PC_6H_5), 135.28 (d, J(PC) 41, *i*-PC_6H_5), 133.96 (d, J(PC) 9.3, *o*- or *m*-PC_6H_5), 130.81 (s, –, *p*-PC_6H_5), 130.16 (s, –, *p*-PC_6H_5), 129.53 (d, ^1J(PC) 51, *p*-PC_6H_5), 127.72 (d, ^3J(PC) 9.2, *m*- or *o*-PC_6H_5), 127.38 (d, ^3J(PC) 10, *m*- or *o*-PC_6H_5), 127.43, 126.12, 125.44 (CC_6H_5), 98.42 (s, –, $C_5(CH_3)_5$), 54.93 (d, ^3J(PC) 8.7, OCH_3), 54.11 (d, ^3J(PC) 9, OCH_3), 50.75 (d, ^2J(PC) 11.0, C*), 27.47 (d, ^2J(PC) 5.7, $C^{\star}CH_3$), 10.25 (s, –, $C_5(CH_3)_5$). IR (CH_2Cl_2) cm^{-1} (intensity, assignment): 1121 (s, ν(P=O)), 1040, 1013 (s, δ(P–O–C)).

Slow cooling of samples of chromatographically enriched high R_f dimethylphosphonate product resulted in formation of crystals of the less soluble, low R_f $(-)_{436}$-**10b** diastereomer. Repetitive preparative thin layer chromatography of the mother liquors from toluene recrystallization attempts afforded highly enriched samples of $(+)_{436}$-**10a** which were used for all spectroscopic measurements. $[\alpha]_{365} = -3591$, $[\alpha]_{436} = +2870$; MS (FAB/glycerol/PTSA) identical with $(-)_{436}$-**10b**; ^1H NMR (CD_2Cl_2), δ (multiplicity, coupling in Hz, rel. integration, assignment): 2.83 (m, 2H, *o*-PC_6H_5), 7.53 (m, 5H, PC_6H_5), 7.18 (m, 3H, PC_6H_5), 7.07 (m, 5H, $C^{\star}C_6H_5$), 6.46 (dd, ^2J(PH) 15.8, ^3J(HH) 8.5, 1H, NH), 3.77 (d, ^3J(PH) 9.6, 3H, OCH_3), 3.64 (d, ^3J(PH) 10.9, 3H, OCH_3), 3.62 (m, 1H, C*H), 1.39 (t, ^4J(PH) 1.4, 15H, $C_5(CH_3)_5$), 0.96 (d, ^3J(HH) 6.8, 3H, $C^{\star}CH_3$); $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ (multiplicity, coupling constant in Hz, assignment): 147.37 (s, –, *i*-$C^{\star}C_6H_5$), 136.83 (d, J(PC) 9.8, *o*- or *m*-PC_6H_5), 135.88 (d, ^1J(PC) 45, *i*-PC_6H_5), 133.79 (d, J(PC) 10.2, *o*- or *m*-PC_6H_5), 131.42 (s, –, *p*-PC_6H_5), 130.39 (d, ^1J(PC) 44, *i*-PC_6H_5), 129.57 (s, –, *p*-PC_6H_5), 128.01 (s, –, $C^{\star}C_6H_5$), 127.84 (d, J(PC) 9.7, *m*- or *o*-PC_6H_5), 126.83 (d, J(PC) 10.4, *m*- or *o*-PC_6H_5), 126.72 (s, –, $C^{\star}C_6H_5$), 126.14 (s, –, $C^{\star}C_6H_5$), 98.23 (s, –, $C_5(CH_3)_5$), 54.67 (d, ^3J(PC) 8.5, OCH_3), 54.27 (d, ^3J(PC) 12, OCH_3), 50.70 (d, ^2J(PC) 10.7, C*), 26.59 (d, ^3J(PC) 6.0, $C^{\star}CH_3$), 10.32 (s, –, $C_5(CH_3)_5$); IR (CH_2Cl_2) identical with $(-)_{436}$-**10b**.

Results and discussion

Synthesis and characterization of ***10a,10b***. Initial attempts to prepare the Cp* analogs of the dimethylphosphonate complex **1** via the sequence **5** → **6** → **10a,10b** (cf. Scheme 1) successfully used previously [1] proved unsatisfactory. Under a variety of conditions substitution of CO in **5** by (*S*)-(−)-diphenyl-1-phenylethylaminophosphine led to complex reaction mixtures. Others have also noted that the substitution chemistry of the isostructural complexes **1** and **5** is divergent, particularly when the steric requirement of the entering ligand is large. Carbon monoxide substitution in **5** by triphenylphosphine, which has steric requirements similar [17] to (*S*)-(−)-diphenyl-1-phenylethylaminophosphine, has been reported to give moderate yields of the $Cp^{\star}CoI_2(PPh_3)$ in refluxing THF but complicated reaction mixtures in less polar solvents [18]. In a related result Fairhurst and White [19] found that no reaction of **5** with triphenylphosphine occurred at room temperature and that complex reaction mixtures resulted on extended reflux.



$Cp^* = \eta^5 - C_5Me_5$; $PNH^* = (S) - Ph_2 PNH \overset{*}{C}H(Me)Ph$

Scheme 1

A ^1H NMR experiment in which (*S*)-(−)-diphenyl-1-phenylethylaminophosphine was added to a solution of **5** in $CDCl_3$ demonstrated that an equilibrium was rapidly established between **5** ($\delta(Cp^*)$ 2.23), its CO substitution product **6** ($\delta(Cp^*)$ 1.65; d, $J(PH)$ 0.9), and the bis-μ-iodo dimer **7** ($\delta(Cp^*)$ 1.82) formed by (*S*)-(−)-diphenyl-1-phenylethylaminophosphine dissociation (cf. Scheme 1). The equilibrium shifted towards **6** in the presence of excess (*S*)-(−)-diphenyl-1-phenylethylaminophosphine. Mixtures of **6** and **7** could be obtained by crystallization. However, attempted chromatographic separation of the product resulted in nearly complete conversion to the dimer **7**. The observed lability of the Co–P bond in **6**, no doubt steric in origin, frustrated in situ preparation of **10a,10b** by addition of $P(OMe)_3$ to solutions of **5** and (*S*)-(−)-diphenyl-1-phenylethylaminophosphine. The major product isolated under these conditions was always **8**, the result of (*S*)-(−)-diphenyl-1-phenylethylaminophosphine rather than iodide substitution.

These results suggested that the inverse procedure **5** → **8** → **10a,10b** (cf. Scheme 1) might provide an alternative synthetic route. Firstly, the steric requirement of $P(OCH_3)_3$ is considerably less than that of (*S*)-(−)-diphenyl-1-phenylethylaminophosphine, hence CO substitution should occur readily. Secondly, although the expected cationic intermediate [20,21,22,23,4] certainly suffers acute steric

congestion, ensuing intramolecular hydrogen bonding [1], which develops during dealkylation, might to some degree "anchor" the labile (*S*)-(−)-diphenyl-1-phenylethylaminophosphine ligand.

This analysis proved successful and good yields of **8**, which is stable toward phosphite dissociation, were obtained on reaction of **5** with $P(OCH_3)_3$. ^1H NMR analysis of the reaction of **8** with (*S*)-(−)-diphenyl-1-phenylethylaminophosphine demonstrated that the reaction is complex and that a number of side products in addition to **10a,10b** are formed. Both iodide and $P(OCH_3)_3$ of **8** appear labile with respect to substitution by (*S*)-(−)-diphenyl-1-phenylethylaminophosphine in methylene chloride. Resonances tentatively assigned to the unstable cationic intermediate **9** were directly observed under suitable conditions. A significant amount of **6** was also found but no free $P(OCH_3)_3$ expected from the substitution **8** → **6** was detected. It is likely that free phosphite would react with **8** to give $[Cp^*CoI(P(OCH_3)_3)_2]^+$ and its Arbuzov product $[Cp^*CoI(P(OCH_3)_3)(P(O)(OCH_3)_2)$. ^1H NMR analysis of the reaction of **8** with (*S*)-(−)-diphenyl-1-phenylethylaminophosphine at low % conversion showed that the diastereomeric phosphonate products were formed in a constant ratio of ca. 2.5/1. When formed **10a,10b** are stable toward (*S*)-(−)-diphenyl-1-phenylethylaminophosphine dissociation (vide in fra) hence they can be easily isolated.

The two diastereomeric phosphonates **10a,10b** formed in the sequence of Scheme 1 are sufficiently configurationally stable at Co to allow separation by a combination of chromatography and fractional crystallization. Optically pure, low R_f product ($(-)_{436}$-**10b**), identical with the major phosphonate kinetic product, is considerably less soluble in toluene/hexane and was readily obtained. The higher R_f product ($(+)_{436}$-**10a**) could not be crystallized but highly enriched samples were obtained chromatographically (cf. experimental). Samples of either diastereomer were found to be configurationally stable in methylene chloride at 38°C for extended periods.

The structure of the dimethylphosphonate complexes **10a,10b** was confirmed spectroscopically (cf. Experimental) and in the case of $(-)_{436}$-**10b** by crystallography. Both epimers exhibit strong, characteristic [24,25] ν(P=O) at ca. 1120 cm^{-1}. The ^1H NMR spectrum of **10a,10b** shows the diastereotopic $POCH_3$ groups as two well resolved doublets with distinctly different, solvent dependent chemical shifts. In very pure samples the NH proton appears as a well resolved double doublet (^2J(PH), ^3J(HH)) at very low field (δ 6.46 and 6.47 for **10a** and **10b**, respectively). The concentration independent, highly deshielded NH resonance observed for both epimers **10a,10b**, compared to the value of δ 2.96 [1] found for η^5-$C_5H_5CoI_2$((*S*)-(−)-diphenyl-1-phenylethylaminophosphine), is consistent with the presence of a strong intramolecular hydrogen bond. The ^1H NMR spectrum of less pure samples, which appeared to epimerize more readily, showed an ill-resolved, slightly shifted NH resonance.

Chiroptical properties and absolute configuration. Circular dichroism (CD) spectra of diasteromerically pure $(-)_{436}$-**10b** and highly enriched samples of $(+)_{436}$-**10a** (cf. Fig. 1) were quasi mirror images as is typically found for transition metal epimeric chiral piano stool complexes [26]. Previously we demonstrated that the morphology of CD spectra is a reliable indicator of absolute configuration at the metal [1] for isostructural series. The CD spectrum of low R_f $(-)_{456}$-**10b** (cf. Fig. 1) was found to be isomorphous with the CD spectrum of the lower R_f diastereomer

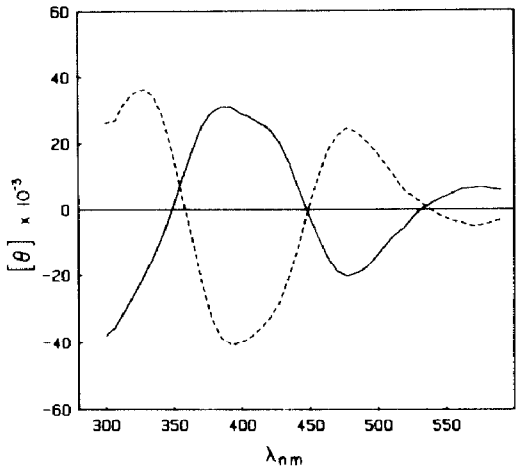


Fig. 1. Circular dichroism spectra of $(+)_{436}$-**10a** (solid line) and $(-)_{436}$-**10b** (dotted line) in toluene.

of its η^5-C_5H_5 analog, R_{Co},S_C-**3** ($R' = OCH_3$, $R = CH_3$) [1] and therefore can be tentatively assigned an identical absolute configuration at cobalt. Using the conventional CIP [27] *R,S* nomenclature generally applied to chiral piano stool complexes [28,29] and the ligand priority sequence I > Cp* > P(O)$(OCH_3)_2$ > (*S*)-(−)-diphenyl-1-phenylethylaminophosphine, the absolute configuration of $(-)_{436}$-**10b** can be specified as R_{Co}. Confirmation of this assignment was obtained crystallographically using Rogers' η method [15] to assign the absolute configurations at Co and C in a single crystal of $(-)_{436}$-**10b**. Figure 2 shows that the absolute configuration of $(-)_{436}$-**10b** is R_{Co},S_C in agreement with the CD spectrum and the known configuration at carbon.

Solid-state structure and conformation of $(-)_{436}$-***10b***. Figure 2 shows the single crystal X-ray structure obtained for $(-)_{436}$-**10b**, which confirms the formulation of **10** as a piano stool dimethylphosphonate complex. If Cp* is considered to occupy three coordination sites, the coordination geometry is pseudo-octahedral with bond angles between monodentate ligands approaching 90° (cf. Table 1). Except for a slight lengthening of the Co–C_{ring} (2.124 vs. 2.089 Å average), Co–PN (2.237 vs.

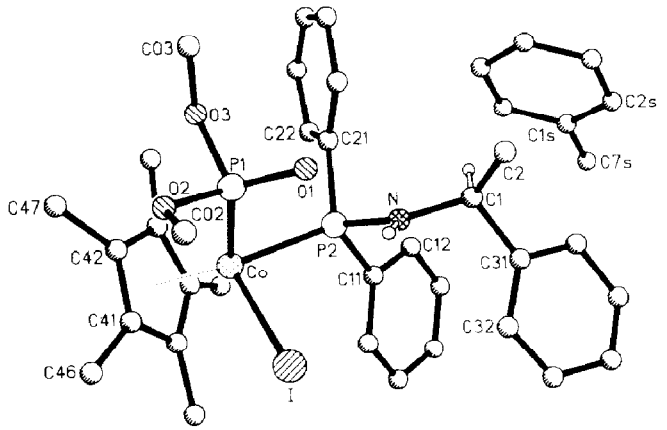


Fig. 2. Molecular geometry and absolute configuration of $(-)_{436}$-**10b**.

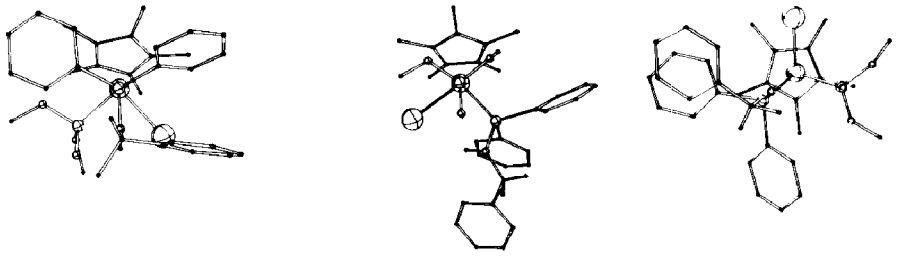


Fig. 3. ORTEP drawings of Newman projections along P(N)–Co, P(O)–Co, and Co–Cp* (centroid) for $(-)_{436}$-**10b**.

2.211 Å), and Co–I (2.585 vs. 2.572 Å), due to the increased steric demands and stronger donor characteristics of Cp* vs. Cp, the overall structure is very similar to **3** ($R' = OCH_3$, $R = CH_3$) [1] and to other related Co^{III} dimethylphosphonate complexes [30,3]. The geometry about the phosphonate P atom is characteristically deformed from tetrahedral. The Co–P=O bond angle opens to ca. 120° with a concomitant closing of the Co–P–O and O–P–O angles. As found for other phosphonate complexes [1] the diastereotopic methoxy groups show different Co–P–O bond angles. This feature of coordinated phosphonate structure persists even when a symmetry plane is present [3,30,31] and most probably derives from solid state conformational preferences.The P=O bond length in $(-)_{436}$-**10b**, which has a strong secondary interaction with N–H (cf. discussion below), is remarkably similar to that of other phosphonate complexes with [1,30,31] or without [3] hydrogen bonding interactions.

Figure 3 shows Newman projections of $(-)_{436}$-**10b** along the P(2) – Co, P(1) – Co, and Co–Cp* (centroid) bonds. The solid state conformation of $(-)_{436}$-**10b** is dominated by the presence of a quasi-boat 6-ring with pseudo-axial iodide and

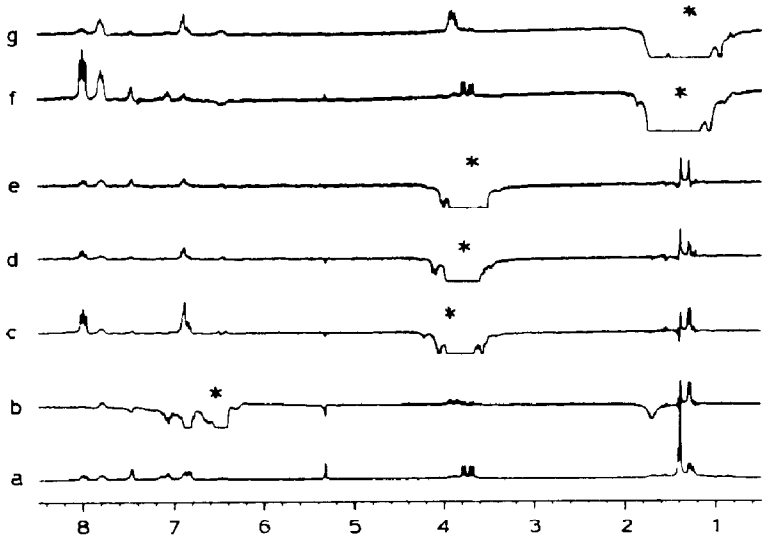


Fig. 4. Proton NOED spectra for $(-)_{436}$-**10b** in CD_2Cl_2: (a) reference spectrum; (b–g) difference spectra ×64 for irradiation at the indicated (*) frequency: (b) NH; (c) C*H; (d) OCH_3; (e) OCH_3; (f) Cp*; (g) C*CH_3.

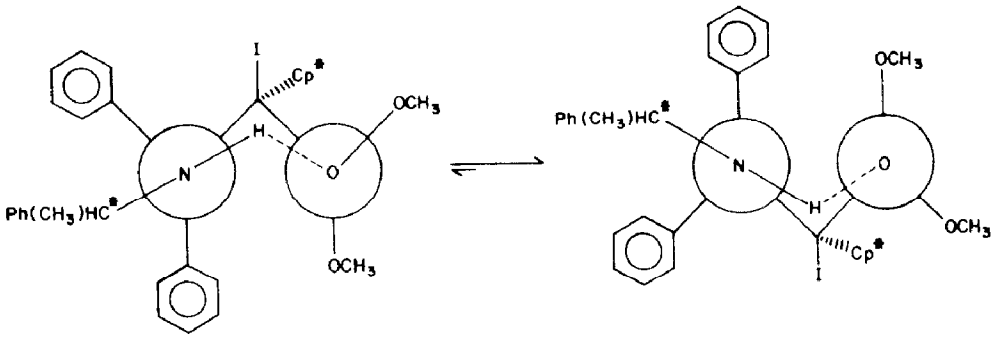


Fig. 5. Newman projections of proposed solution conformation for $(-)_{436}$-**10b**.

pseudo-equatorial Cp* which is established by a strong, intramolecular P=O · · · HN hydrogen bond similar to that found previously for the related phosphonate and phosphinate complexes **3**. Refinement with idealized N–H bond distance gives values of 2.151 and 2.759 Å for H · · · O(1) and N · · · O(1) respectively which are well within the range considered indicative of a strong NH · · · O hydrogen bond [32]. The aminophosphine nitrogen atom is very nearly planar and in order for the CH(Me)Ph group to assume a staggered conformation between the phosphine phenyl groups, the N–H eclipses with the P–Co bond resulting in the observed quasi-boat conformation. As a consequence of intramolecular hydrogen bonding the Cp* ring and P(2) are forced *trans* rather than the more commonly observed *gauche* orientation [33].

Solution conformation. The solution conformation of $(-)_{436}$-**10b** was investigated in methylene chloride-d_2 using ^{1}H nuclear Overhauser enhancement difference spectroscopy (NOED) [34]. The results shown in Fig. 4 support the conclusion that the conformation observed in the solid state (cf. Fig. 3) also dominates in solution. Our interpretation of the NOED results is based on the model shown in Fig. 5 which retains the intramolecular NH · · · O=P hydrogen bond in solution. The critical results of the NOED experiments are that positive enhancements occur between both diastereotopic *o*-protons of PPh_2 and both diastereotopic OCH_3 groups and the Cp* ring methyl groups. These results suggest that Cp* occupies a pseudo-equatorial position so that it is *gauche* with respect to these groups in the dominant solution conformer. The alternative conformer (cf. Fig. 5) places Cp* pseudo-axial with a *trans* relationship to one member of the diastereotopic PPh_2 and OCH_3 pairs.

Conclusion

The substitution of the sterically more demanding and stronger σ-donor ligand Cp* for Cp in **3** does not appreciably alter the configurational stability, structure or conformation adopted in the solid state and in solution. All structurally analogous 2-aminophosphine phosphonate complexes **3** (Cp = η-C_5H_5, η-$C_5(CH_3)_5$; R = OCH_3, Ph; OR=OCH_3) reported thus far [1] appear to favour a six-membered intramolecular hydrogen bonded (NH · · · O=P) ring conformation, which places the C_5 ring in a pseudo-equatorial position.

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