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Synthesis, structure and reactivity of bidentate 2-ketopyrrolyl cobalt(III) phosphonates and phosphinates

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Abstract

Bidentate N,O complexes $(\eta^3-C_3R_5)Co(R'C(O)-C_4H_3N)(1)$ (3) are prepared by treating in situ produced 2-acyl-pyrrolyl anion $(R'C(O)-C_4H_3N^-, 2\alpha,\beta; \alpha (R'=H), \beta (R'=Me))$ with $(\eta^5-C_3R_5)Co(CO)(1)_2$ (1a,b; a (R=H), b (R=Me)) in THF. Reaction of 3 with P-donor ligands (PMe_3, P(OMe)_3 and PPh(OMe)_2) results in simple halide substitution to give $[(\eta^5-C_3R_5)Co(R'C(O)-C_4H_3N)(P-donor)]^+1^-$ (4-6). The PMe_3 product (4) is readily isolated, however facile Arbuzov dealkylation of the phosphite (5) and phosphonite (6) salts gives dimethyl phosphonates, $(\eta^5-C_3R_5)Co(R'C(O)-C_4H_3N)(P(O)Ph(OMe)_2)$ (7), and mixtures of diastereometic methyl phenylphosphinates, $(\eta^5-C_3R_5)Co(R'C(O)-C_4H_3N)(P(O)Ph(OMe))$ (8), respectively. Intermediate phosphite and phosphonite complexes $[(\eta^5-C_3R_5)Co(R'C(O)-C_4H_3N)(P(O)Ph(OMe))]^+1^-$ (5, 6; R''=OMe, Ph) were directly observed by ¹H NMR in acetone-d₆ at room temperature in several cases. The molecular structures of complexes **3b** β and **7b** β were determined by X-ray diffraction. **3b** β crystallizes in the orthorhombic system with a = 16.809(3), b = 13.755(5), c = 7.535(2) (Å, V = 1742(1) Å³, Z = 4. Although the coordination geometry of **3b** β was determined, disorder problems in the selected crystal prevented refinement of the diffraction data to give meaningful structural parameters. **7b** β crystallizes in the monoclinic system, space group $P2_1/c$ (No. 14) with a = 12.183(1), b = 10.100(2), c = 16.915(2) Å, $\beta = 106.559(9)^\circ$, V = 1995.1(4) Å³, Z = 4 and R = 0.036 ($R_w = 0.039$) for 2716 reflections with $I > 3.00\sigma(I)$. Conformation preferences for modeling (MM +) and extended Hückel calculations.

Keywords: Crystal structures; Cobalt complexes; Phosphonate complexes; Phosphinate complexes

1. Introduction

Polydentate ligands which present both strong and weak Lewis base sites are of current interest in view of their ability to show 'hemilabile' $(\eta^1 \leftrightarrow \eta^2)$ coordination [1-5]. Hemilable P,O ligands which are able to open a coordination site that can readily incorporate substrate into the coordination sphere of the metal, see Eq. (1), can result in a marked increase in selectivity under homogeneous catalytic conditions [4,6-10]. Most effort in this area has focused on neutral P,O ligands but, in principle, late transition metal hemilable coordination should be possible for a wide array of oxygenated Lewis bases L,O and related combination ligands [11].

As part of our continuing studies of ligand sphere effects on metal-to-phosphorus chiral induction in the transition metal Arbuzov reaction (Eq. (2)) we have examined the reaction of several chiral, pseudo-octahedral Co(III) iodides with prochiral dimethyl alkyl- and arylphosphonites [12,13]. Co-chiral auxiliaries containing Brunner's bidentate N,N Schiff base ligands derived from 2-pyrrolecarbaldehyde, (S_c) -Ph(Me)C*HN=CR'-C₄H₃N⁻ (R'=H) [14-18], were found to substitute with complete retention of stereo-chemistry at cobalt, however subsequent Arbuzov chemistry proceeded with only moderate diastereoselectivity at phosphorus [19].

$$\ln M \begin{pmatrix} L \\ 0 \end{pmatrix} \longrightarrow \ln M \begin{pmatrix} L \\ 0 \end{pmatrix} \xrightarrow{+L'} \ln M \begin{pmatrix} L \\ 0 \end{pmatrix} (2)$$

In the course of that work we prepared the potentially hemilabile bidentate N,O⁻ ligands R'C(O)-C₄H₃N⁻ (2α , β : R' = H (α), Me (β)) by proton abstraction from 2ketopyrrole Schiff base precursors. This paper describes the preparation, characterization and chemistry of several new Co(III) complexes in which anionic 2-keto pyrrolyl N,O⁻

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Scheme 1.

ligands $2\alpha,\beta$ demonstrate a strong preference for η^2 coordination and a surprising substitution inertness.

2. Results and discussion

2.1. Synthesis and characterization of $(\eta^5 - C_5 R_5)Co(R'C(O) - C_4 H_3N)(I)$ (3)

 $(\eta^5-C_5R_5)Co(CO)I_2$ (R = H (1a), Me (1b)) reacts with 1 equiv. of 2-acylpyrrolyl anion, R'C(O)-C_4H_3N^- (R' = H

Table 1 Physical properties of $(\eta^{5}-C_{5}R_{5})Co(R'-C(O)-C_{4}H_{3}N)(L)$ complexes

 (2α) , Me (2β)) obtained in situ by treatment of 2-formylpyrrole or 2-acetylpyrrole with NaH in dry THF, to give good yields of the bidentate N,O chelate, $(\eta^5-C_5R_5)$ -Co(R'C(O)C₄H₃N)(I) (3), the product of simple, sequential substitution of CO and I⁻ in the starting complex 1 by $2\alpha,\beta$ (see Scheme 1). The dark blue, crystalline 2-ketopyrrole products 3 are air stable both in the solid state and in solution and are very soluble in benzene, dichloromethane, acetone and methanol, but only slightly soluble in hexane. Assignment of an N,O bidentate pseudo-octahedral pianostool structure 3 is supported by physical properties (Table 1), spectroscopic data (Tables 2 and 3) and solid state X-ray data (Fig. 1), in the case of $3b\beta$.

Analytical (Table 1) and spectroscopic data (Tables 2 and 3) confirm a 1:1 stoichiometry for the isolated iodo Co(III) 2-ketopyrrolyl complexes (3). Proton NMR spectra, assigned by comparison with literature analogs [16], show Cp or CP* resonances at ~5.5 and 1.6 ppm, respectively, as well as multiplets [16,19] for the pyrrole ring protons (H₅ (7.6–8.0 ppm) > H₃ (7.0–7.2 ppm) > H₄ (6.5–6.6 ppm)). Pyrrole ring assignments in complexes of 2α were confirmed

No.	R	R'	L	Formula	Yield ^a (%)	Appearance	М.р. ^ь (°С)	C, H, N (%) Calc. (Found)	$\nu(C=O)/\nu(P=O)$ (cm ⁻¹)
3a <i>a</i>	н	н	I	C10H9NOICo	72	dark blue crystal	136-137	34.81, 2.63, 4.06	1566
3aβ	н	Me	1		78	dark blue crystal	160-161	(34.80, 2.02, 4.02) 36.80, 3.09, 3.90 (36.64, 3.03, 3.97)	1550
3ba	Me	н	I	C15H19NOICo	65	dark blue crystal	187-190	43.40, 4.61, 3.37 (43.33, 4.56, 3.39)	1566
3bβ	Me	Me	I	C16N21NOIC0	75	dark blue prism	205-208	44.78, 4.93, 3.26 (44.68, 4.89, 3.25)	1549
4aβ	н	Me	PMe ₃	C14H20NOPIC0	95	deep red powder	>110 dec.	38.64, 4.63, 3.22 (38.70, 4.64, 3.03)	1554
4ba	Me	н	PMe ₃	C18H28NOPICo	86	deep red powder	157-159	44.01, 5.74, 2.85 (44.35, 5.68, 2.85)	1564
4bβ	Me	Me	PMe ₃	C19H30NOPICo	99	deep red powder	>130 dec.	45.17, 5.98, 2.77 (45.20, 6.16, 2.58)	1551
баβ	H	Me	PPh(OMe) ₂	C ₁₉ H ₂₂ NO ₃ PICo	70	deep red powder	75–77	43.12, 4.19, 2.65 (43.25, 4.15, 2.68)	1555
7a <i>a</i>	н	н	P(O)(OMe) ₂	C12H15NO4PCo	60	red powder	95-97		1566/1157
7aβ	Н	Me	$P(O)(OMe)_2$	C13H17NO4PC0	98	red powder	99-101	45.76, 5.02, 4.11 (45.54, 4.90, 3.81)	1550/1156
7ba	Me	Н	$P(O)(OMe)_2$	C17H25NO4PC0	94	red powder	81-83	51.39, 6.34, 3.53 (51.21, 6.45, 3.39)	1565/1149
7bβ	Me	Ме	P(O)(OMe) ₂	C18H27NO4PC0	93	deep red prism	> 130 dec.	52.56, 6.62, 3.41 (52.55, 6.56, 3.42)	1548/1152
8aα ^c	н	н	P(O)Ph(OMe)	C17H17NO3PCo	71	red crystal			1548/1138
8aβ ^d	н	Me	P(O)Ph(OMe)	C18H19NO3PCo	95	red crystal			1550/1144
8bα °	Me	н	P(O)Ph(OMe)	C22H27NO3PC0	92	red crystal			1564/1136
8bβ '	Me	Me	P(O)Ph(OMe)	C23H29NO3PC0	99	red crystal		60.40, 6.39, 3.06 (60.59, 6.45, 2.98)	1546/1135

* Isolated yield before crystallization.

^b Sealed (N₂) capillary.

^c Mixture of two diastereomers 1/2=57/43.

^d Mixture of two diastereomers 1/2=53/47.

° Mixture of two diastereomers 1/2=51/49.

^r Mixture of two diastereomers 1/2 = 50/50.

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aß ba Mi	H		7.12	6.56	7.62	5.57	8.1		
aß box Mi Mi Mi			(dd, 4.2, 0.8) ^b	(dd, 4,4, 1.4) °	(d, 0.9) ^d	(s)	(d, 1.0) ^c 2, 2, 2		
bæ Mi bß Mi	Me	-	10.7	6.52 144 4 7 1 5 1 5 1 5	8.00 (d 12) d	(3)	76.7		
ρα βββ Wi	5	-	1 0/1 7 0/1	(nn; -1:-; 1:-) 6 57	7.83	1.61	7.90		
bβ Mi	5	-	(dd. 4.2. 0.9) ^b	(dd. 4.2, 1.5) °	(dd, 2.1, 1.2) ^r	(s)	¢(0'0) ¢		
	Me	I	6.95	6.48	7.76	1.64	2.32		
		•	(dd, 4.1, 0.8) ^b	(dd, 4.0, 1.5) °	(d, 1.2) ^d	(s)	(s)		
aß H	Me	PMe,	7.16	6.53	7.89	5.86	2.37	1.54 (d, 12.6) °	26.33
•			(d, 4.3) ^g	(ud, 4.3, 1.2) °	(s)	(s)	(s)		(s)
bar Mi	H	PMe,	7.28	6.63	7.61	1.48	8.22	1.23 (d, 11.1) °	07.cl
		L.	(dt, 4.4, 1.0) ¹	(dd, 4.4, 1.4) °	(s)	(d. 1.8)	(dd, 3.1, 0.8) ⁶		(S) 14 05
ŭb₿ Mi	e Me	PMe ₃	7.16	6.56	7.44	1.48	2.45	1.20 (d, 11.0) "	C6.01
		1	(d, 4.3) ^g	(dd, 5.0, 1.5) °	(q, 0.6) ^d	(d, 1.7) ^J	(s)		(s)
H 'aß'	Me	PPh(OMe) ₂	6.88	6.42	7.87	5.97	1.88	4.05 (d, 12.1)	161.47
•		•	(d, 4.4) ^g	(dd, 4.3, 1.6) °	(d, 0.7) ^d	(2)	(s)	3.96 (d, 11.7) "	(s)
'aor H	н	P(0)(OMe),	7.25	6.47	7.60	5.35	7.90	3.66 (d, 11.1) "	75.83
			(d. 4.2) ^g	(dd, 4.4, 1.4) °	(8)	(s)	(dd, 3.6, 0.7) *	2.97 (d, 9.9) "	(s)
'a <i>B</i> H	Me	P(O)(OMe),	7.14	6.41	7.50	5.33	2.33	3.65 (d, 10.6) "	77.34
+			(dd. 4.2. 0.5) ^b	(dd, 4.2, 1.4) ^c	(S)	(s)	(S)	2.93 (d, 9.4) ^m	(s)
'ba	H	P(O)(OMe),	(() 1.17	6.47	7.46	1.47	8.19	3.59 (d, 10.8) ^m	87.61
	:		(d. 4.2) B	(dd. 4.2, 1.3) °	(s)	(6'1'P)	(dd, 3.7, 0.7) *	2.76 (d, 9.5) ^m	(s)
ma M	e Me	P(O)(OMe).	1.07	6.40	7.37	1.47	2.36	3.54 (d, 10.6) ^m	88.95
			(dt. 4.1. 0.7)	(dd, 4.1, 1.5) °	(d. l.1) d	(d, 2.0) ^J	(s)	2.77 (d, 9.6) "	(s)
kao-1° H	H	P(O)Ph(OMe)	6.91	6.42	7.49	5.19	7.54	3.31 (d, 10.5) "	100.20
	:		((4.4.3))	(dd, 4.3, 1.3) °	(S)	(s)	(d. 2.9) °		(s)
kao-2 "H	H	P(O)Ph(OMe)	6.71	6.34	7.49	5.32	7.49 "	3.77 (d, 10.7) "	104.90
	:		(4.4.3) 8	(dd. 4.3, 1.2) °	(S)	(s)			(s)
laß-1 ^p H	Me	P(O)Ph(OMe)	6.81	6.36	7.42	5.23	1.81	3.42 (d, 10.5) ^m	104.74
	l		(dd. 3.9. 0.5) ^b	(dd, 4.2, 1.4) °	(s)	(s)	(s)		(s)
Jad-2P H	Me	P(O)Ph(OMe)	6.60	6.29	7.39	5.32	1.91	3.80 (d, 11.5) "	107.55
•			(d, 4.2) ^g	(dd, 4.0, 0.5) °	(s)	(s)	(s)		(s)
3ba-1 ° M	e H	P(O)Ph(OMe)	6.78	6.42	7.42	1.41	7.63	3.33 (d, 10.4) "	108.70
		•	(d, 4.2) ^g	(dd, 4.2, 1.4) °	(t, 0.9) ^f	(q. 1.6) ^J	(dd, 3.4, 0.9) ^k		(s)
8ba-24 M	e H	P(O)Ph(OMe)	6.55	6.31	7.37	1.48	7.46	3.66 (d, 10.6) "	110.85
			(d, 4.2) ^B	(dd, 4.2, 1.4) °	(t, 0.9) ^r	(q, 1.6) ^j	(dd, 3.1, 0.9) *		(S)
8b.8-1 M	e Me	P(O)Ph(OMe)	6.62	6.34	7.32	1.1	1.83	3.43 (d. 10.3)	110.76
			(d, 4.1) ^g	(dd, 4.1, 1.4) °	(d, 0.6) ^d	(q, 1.6) ^j	(s)		(s)
8b/8-2' M	le Me	P(O)Ph(OMe)	6.44	6.23	7.29	1.48	1.87	3.66 (d, 10.10) 3.66	14.211
			(d, 4.1) ⁸	(dd, 4.1, 1.4) °	(d, 0.9) ^d	(d, 1.6) ^J	(S)		(8)
								1040	tinlet: a - cinclet.

Table 2

by nuclear Overhauser effect difference (nOed) experiments which consistently gave ~ 12% enhancements of the 7.0-7.2 ppm signal assigned to pyrrolyl H₃ on partial saturation of the formyl resonance. Selective saturation of the H₃ resonance gave enhancements of CHO and the highest field pyrrole ring signals which was then assigned as H₄. Coordination of the formyl oxygen in 2α results in a substantial bathochromic shift of ν (C=O) (2 α , 1601 cm⁻¹; 3a α and 3b α , 1566 cm⁻¹) and a large upfield CHO ¹H NMR shift (-0.78 and -0.98 ppm for $3a\alpha$ and $3b\alpha$, respectively). A much smaller decrease in ν (C=O) frequency was observed on complexation of the 2-acetylpyrrolyl anion (2 β , 1567 cm⁻¹; 3a,b β , 1550, 1549 cm⁻¹). Bidentate coordination of the ligands $2\alpha,\beta$ results in comparatively small ¹³C NMR complexation shifts (Table 3). ¹³C NMR chemical shifts for C₂ and C₅, assigned on the basis of 2-D ¹H/¹³C ¹J heterocorrelation experiments, appear at lower field (~144-149 ppm) than C3 and C4 (120-125 and 117-119 ppm, respectively).

2.2. Molecular structure of 3b B

A single crystal X-ray structure was carried out on complex **3b** β in order to confirm the spectroscopically established bidentate coordination of ligand 2β . Structure refinement for

Table 3 ¹³C NMR data for (n⁵-C₅R₅)Co(R'-C(O)-C₄H₃N)(L) complexes ^a



Fig. 1. PLUTO representation of $(\eta^5-C_5Me_5)Co(MeC(O)-C_4H_3N)(1)$ (3bB).

complex $3b\beta$ in space group *Pnma* was complicated by the presence of a rotationally disordered pentamethylcyclopentadienyl group and by positioning of the molecule on a mirror

No	R	R'	L	<u>с</u> ,	C,	C.	C.	C=0	 CR'=0	Cp/Cp*	Cp-R	P-Me/P-OMe
					,					•••	•	
3aα	н	н	I	145.98	125.15	119.68	149.21	181.68		83.03		
3aβ	н	Me	I	144.22	122.90	118.04	147.00	193.34	21.38	82.88		
3ba	Me	н	I	145.43	123.87	118.70	144.70	179.38		91,24	10.41	
3bβ	Me	Me	I	143.79	121.65	117.10	142.75	190.85	21.91	91.07	10.40	
4aβ	н	Me	PMe ₃	144.54	123.84	119.58	149.44	193.47	21.23	87.91		15.06 (d, 29.1) ^b
4bβ	Me	н	PMe ₃	146.40	125.88	120.66	145.78	180.55		96.52	9.69	12.12 (d, 29.6) ^b
4bβ	Me	Me	PMe ₃	144.26	123.59	119.04	143.30	192.44	22.23	96.27	9.56	12.06 (d, 30.0) ^b
6aβ°	н	Me	PPh(OMe) ₂	147.33	123.92	119.65	150.23	192.94	20.64	89.00		57.26 (d, 8.3) ^d
												56.55 (d, 9.4) ^d
7aα	н	Н	$P(O)(OMe)_2$	146.55	123.95	118.36	150.13	182.40		86.91		51.50 (d, 9.8) ^d
7aβ	н	Me	$P(O)(OMe)_2$	144.69	121.54	116.61	147.99	194.09	21.19	86.77		51.39 (d, 6.4) ^d
7bα	Me	н	$P(O)(OMe)_2$	145.97	122.90	117.56	144.78	180.51		95.10	8.84	50.37 (d, 8.7) ^d
7bβ	Me	Me	$P(O)(OMe)_2$	144.20	120.51	115.84	142.86	192.01	21.89	94.92	8.91	50.31 (d, 7.7) ^d
8aα-1 °	н	н	P(O)Ph(OMe)	145.95	123.87	118.29	149.52	181.90		87.39		51.07 (d, 9.1) ^d
8aα-2 '	н	н	P(O)Ph(OMe)	145.39	123.87	118.71	149.52	181.24		87.21		52.29 (d, 12.2) d
8aβ-1 ⁸	н	Me	P(O)Ph(OMe)	144.57	121.47	116.62	147.28	193.29	20.73	87.20		51.10 (d, 7.5) ^d
8aß-2 8	н	Me	P(O)Ph(OMe)	144.25	121.54	117.11	147.51	192.47	20.65	87.04		52.01 (d, 7.3) ^d
8bα-1 h	Me	н	P(O)Ph(OMe)	145.95	123.06	117.64	144.08	179.74		94.81	8.69	50.35 (d, 11.6) ^d
8bα-2 '	Me	н	P(O)Ph(OMe)	145.39	122.86	117.93	144.08	179.40		94.81	8.69	51.43 (d, 11.5) ^d
8bβ-1 ^j	Me	Me	P(O)Ph(OMe)	144.12	120.67	115.90	141.98	191.21	21.29	94.66	8.69	50.55 (d, 11.6) d
8bβ-2 *	Me	Me	P(O)Ph(OMe)	143.74	120.52	116.20	141.98	190.64	21.70	94.66	8.69	51.24 (d, 11.9) ^d

^{a 13}C NMR (75.47 MHz) chemical shifts in ppm relative to solvent CDCl₃ = 77.00; d = doublet; J values in Hz given in brackets.

^b P-Me, ¹J(PC).

^c Phenyl carbons: 147.49 (C_{ipso}); 132.64 (C_{para}); 130.35, 130.20 (C_{ortho}); 128.82, 128.66 (C_{meto}).

^d P-OMe, ²J(PC).

- ^e Phenyl carbons: 129.76 (Control); 129.61 (Control and Course); 127.58, 127.44 (Control).
- ¹ Phenyl carbons: 130.30, 130.17 (Cortho); 129.39 (Cpare); 127.11, 126.98 (Cmeta).

⁸ Phenyl carbons: 127.35-129.79.

- ^h Phenyl carbons: 137.03 (d, 40.7, Cipto); 130.20, 130.05 (Cortho); 128.40 (Cpara); 126.45, 126.33 (Cmeta).
- ¹ Phenyl carbons: 135.40 (d, 43.6, C_{low}); 130.20, 130.05 (C_{orthe}); 128.17 (C_{pare}); 126.71, 126.61 (C_{metal}). ¹ Phenyl carbons: 137.07 (d, 39.8, C_{love}); 129.57, 129.41 (C_{arthe}); 128.03 (C_{pare}); 126.49, 126.34 (C_{metal}).
- ^k Phenyl carbons: 136.23 (d, 40.2, C_{ipto}); 129.88, 129.72 (C_{ortho}); 128.22 (C_{para}); 126.61, 126.49 (C_{meta}).



Fig. 2. Resonance structures for the 2-ketopyrroiyi anion.

plane with Co and I atoms in the plane. Both enantiomers are evidently able to occupy the same position in the unit cell. This surprising observation was confirmed by solutions in space groups of lower symmetry, notably $Pna2_1$. We are unable to distinguish random occupancy of the site from an alternative in which the enantiomers occupy different growth zones in the crystal. The latter case would, however, require a continuous lattice with very little misalignment between zones and therefore appears unlikely. Although the coordination geometry of $3b\beta$ was clear, we were not able to refine the diffraction data to give meaningful structural parameters. Fig. 1 shows a PLUTO representation of the molecular structure obtained which is a typical pseudo-octahedral three-legged piano-stool with bidentate 2-acetyl pyrrolyl ligand, 2β , as inferred from spectroscopic evidence.

IR spectra show large bathochromic ν (C=O) shifts of 65 and 90 cm⁻¹ on deprotonation of 2α -H and 2β -H, respectively, suggesting substantial delocalization of negative charge onto oxygen in the uncoordinated N,O⁻ pyrrolyl anions 2α and 2β . Extended Hückel calculation of atom charges at the N and O donor sites of $2\alpha/2\beta$ give -1.041/-1.044and -1.204/-1.220, respectively. Increased importance of resonance structure 2" in the pyrrolyl anion compared to its conjugate acid (see Fig. 2) rationalizes both the IR data and the propensity for bidentate N,O coordination found in this study. The coplanar, five-membered chelate (Co(1)-O(1)-C(15)-C(14)-N(1)) and pyrrolyl rings [19,20] in the bidentate N,O complex permits extensive π -conjugation over the entire sp² network allowing considerable charge delocalization at oxygen.

2.3. Substitution reactions of $(\eta^{5}-C_{5}R_{5})Co(R'C(O)-C_{4}H_{3}N)(I)$ with PMe₃

Complexes **3a** β , **3b** α and **3b** β were treated with PMe₃ in order to probe the substitution lability of the bidentate, N,O⁻ 2-formyl- and 2-acetylpyrrolyl ligands. Although extended (>24 h) reflux of **3** in benzene with excess (×10) PMe₃ eventually led to decomposition with no observable Cp or Cp* containing products, shorter term reaction (see Scheme 1) at room temperature or under reflux gave only the monosubstituted cation, [(η^5 -C₃R₃)Co(R'C(O)-C₄H₃N)(PMe₃)]⁺I⁻ (**4a** β , **4b** α and **4b** β), the result of simple iodide substitution. The structure of **4** follows from analytical (Table 1) and spectroscopic data (Tables 2 and 3). Characteristic signals for coordinated PMe₃ were observed by ¹H NMR (1.54 ppm for **4a** and 1.2 ppm for **4b**) and ³¹P NMR (26.3 ppm for **4a** and ~ 15.20 and 16.95 for 4b derivatives). NMR reactions of complexes $3a\beta$, $3b\alpha$ or $3b\beta$ with excess (×10) PMe₃ in acetone-d₆ at room temperature showed that $4a\beta$, $4b\alpha$ or $4b\beta$ were the only observed products after several hours subsequent to disappearance of reactant. No reaction occurred when $4a\beta$, $4b\alpha$ or $4b\beta$ was treated with sodium iodide in acetone-d₆ at room temperature or at 45 °C hence iodide substitution is irreversible. Unlike related bifunctional acyl phosphines [4-6], complexes of $2\alpha,\beta$ do not appear to be hemilabile.

2.4. Reaction of $(\pi^{5}-C_{5}R_{5})Co(R'C(O)-C_{4}H_{3}N)(I)(3)$ with $P(OMe)_{3}$

Trimethylphosphite also reacts with 3 via initial iodide substitution, however the resulting cationic complex 5 undergoes subsequent Arbuzov dealkylation with the elimination of methyl iodide to give 7. Reaction of $3a\alpha$ and $3a\beta$ with excess P(OMe)₃ in benzene at room temperature for 12 h gave dimethyl phosphonate products, $(\pi^5-C_5H_5)$ - $C_0(R^{\circ}C(0)-C_4H_3N)P(0)(OMe)_2)$ (7aa, 7a β) which were isolated as red solids (see Scheme 1). Physical properties and spectroscopic data are presented in Tables 1-3. Metallophosphonate formation was evidenced by the presence of two diagnostic ¹H NMR methoxy doublets $({}^{3}J(PH) = 11.0 \pm 1.5)$ at 2.9-3.7 ppm assigned to the diastereotopic P(O) (OMe)₂. IR spectra showed a strong metallophosphonate ν (P=O) band [21-24] at 1149-1157 cm⁻¹ as well as a medium intensity ν (C=O) at 1548-1566 cm⁻¹ consistent with retention of bidentate ligand coordination. Cationic intermediates $[(\eta^5-C_5H_5)Co(R'C(0)-C_4H_3N) (P(OMe)_3)$ ⁺ (5a α , 5a β), observed by ¹H NMR spectroscopy in acetone-d₆ (5aα, Cp: 5.81 ppm, P(OMe)₃: 3.80 ppm (d, 10.5 Hz); 5aβ, Cp: 5.80 ppm, P(OMe)₃; 3.77 ppm (d, 10.9 Hz)) indicate a sequential substitution mechanism [19,21,22,25-27]. Reaction of $(\eta^5-C_5Me_5)C_0(R'C(O) C_{4}H_{3}N(I)$ (3ba, 3b β) with excess P(OMe)₃ proceeded with difficulty [28] requiring prolonged reflux in benzene to form the analogous phosphonates $(\pi^5 - C_{\star}Me_{\star})Co(R'C(O) C_4H_3N$ (P(O) (OMe)₂) (7ba, 7b β) which were characterized by analytical and spectroscopic data (Tables 1-3) as well as by a single crystal X-ray study in the case of $7b\beta$.

2.5. Molecular structure of $(\pi^5 - C_5 Me_5)Co(MeC(O) - C_4H_3N)(P(O)(OMe)_2)(7b\beta)$

A deep red single crystal was grown by slow diffusion of hexane onto a solution of **7b** β in chloroform. A PLUTO representation of the three-legged piano-stool molecular structure obtained by refinement of X-ray diffraction data is shown in Fig. 3. Tables 4 and 5 give selected bond distances and bond angles, and atomic coordinates. The cobalt atom in **7b** β demonstrates a distorted octahedral coordination sphere with η^5 -C₅Me₅ occupying three *fac* coordination sites. The remaining coordination sites are filled by a P-phosphonate and a bidentate, planar [19,20] 2-acylpyrrolyl ligand. Bite angle requirements of **2** β reduce the O(4)-Co(1)-N(1)

Table 5 Atomic

coordinates

for



Fig. 3. PLUTO representation of $(\eta^5-C_5Me_5)Co(MeC(O)-C_4H_3N)-(P(O)(OMe)_2)$ (7b β).

Table 4		
Selected bond distances (Å)) and bond angles ((°) for complex 7bß

Bond distances		
Co(1)-P(1)	2.195(1)	
Co(1)-O(4)	1.970(2)	
Co(1)-N(1)	1.928(3)	
Co(1)-C(1)	2.077(3)	
Co(1)-C(2)	2.039(3)	
Co(1)-C(3)	2.126(4)	
Co(1)-C(4)	2.110(4)	
Co(1)-C(5)	2.058(3)	
P(1)-O(1)	1.481(3)	
P(1)-O(2)	1.610(3)	
P(1)-O(3)	1.613(3)	
O(4)-C(15)	1.274(4)	
N(1)-C(14)	1.392(4)	
C(14)-C(15)	1.395(5)	
C(15)-C(16)	1.500(5)	
Bond angles		
P(1)-Co(1)-O(4)	92.34(8)	
P(1)-Co(1)-N(1)	90.37(9)	
O(4)-Co(1)-N(1)	83.1(1)	
Co(1)-P(1)-O(1)	118.3(1)	
Co(1)-P(1)-O(2)	104.6(1)	
Co(1)-P(1)-O(3)	110.5(1)	
Co(1)-O(4)-C(15)	112.3(2)	
Co(1)-N(1)-C(11)	142.1(3)	
Co(1)-N(1)-C(14)	111.4(2)	
N(1)-C(14)-C(15)	114.3(3)	
O(4)-C(15)-C(14)	118.7(3)	

angle to 83.1° however the remaining interligand angles (P(1)-Co(1)-N(1)=90.37(9), P(1)-Co(1)-O(4)=92.34(8)) are not appreciably distorted from the normal octahedral values. The P(1)-O(1) bond length of 1.481(3) Å is unremarkable.

2.6. Metallophosphonate conformation and bonding: extended Hückel and molecular modeling studies

Widespread interest in applications of stereo directing properties of pseudo-octahedral chiral-at-metal fragments

(OMC)2)(/0p)			
Atom	x	у	z	Beq
Co(1)	0.28185(4)	0.01249(5)	0.28234(3)	2.35(2)
P(1)	0.16016(9)	0.1284(1)	0.18665(6)	3.26(4)
0(1)	0.2040(3)	0.2003(3)	0.1256(2)	5.1(1)
O(2)	0.0595(2)	0.0256(3)	0.1444(2)	4.7(1)
O(3)	0.0875(2)	0.2270(3)	0.2275(2)	4.1(1)
O(4)	0.1710(2)	-0.0095(2)	0.3464(1)	3.1(1)
N(1)	0.3241(2)	0.1691(3)	0.3492(2)	2.6(1)
C(1)	0.3215(3)	-0.1034(4)	0.1928(2)	3.0(2)
C(2)	0.4184(3)	-0.0289(4)	0.2394(2)	3.1(2)
C(3)	0.4474(3)	-0.0743(4)	0.3231(2)	3.1(2)
C(4)	0.3649(3)	-0.1661(4)	0.3295(2)	3.1(2)
C(5)	0.2847(3)	-0.1833(3)	0.2492(2)	3.1(2)
C(6)	0.2753(4)	-0.1073(5)	0.1002(2)	5.1(2)
C(7)	0.4836(4)	0.0702(4)	0.2047(3)	5.0(2)
C(8)	0.5501(4)	-0.0295(5)	0.3904(3)	5.4(2)
C(9)	0.3566(4)	-0.2336(4)	0.4071(3)	5.2(2)
C(10)	0.1835(4)	-0.2757(4)	0.2286(3)	5.4(2)
C(11)	0.3945(3)	0.2729(4)	0.3614(2)	3.6(2)
C(12)	0.3820(4)	0.3501(4)	0.4276(3)	4.1(2)
C(13)	0.3001(4)	0.2909(4)	0.4566(2)	3.8(2)
C(14)	0.2638(3)	0.1782(4)	0.4076(2)	2.9(1)
C(15)	0.1819(3)	0.0793(4)	0.4016(2)	3.3(2)
C(16)	0.1056(4)	0.0726(5)	0.4572(3)	5.6(2)
C(17)	-0.0425(4)	0.0719(6)	0.0856(3)	7.2(3)
C(18)	0.1129(4)	0.3655(5)	0.2360(3)	6.0(2)

 $(\pi^{5}-C_{s}Me_{s})Co(Me-C(O)-C_{a}H_{3}N)(P(O$

[29-32] has necessitated detailed conformational analyses of piano-stool molecules of the type CpM(L)(X)(P-donor) [33-41]. Three-fold M-X rotational barriers for X = alkyl have been successfully interpreted [34-38] primarily on the basis of steric effects taking into account the pseudo-octahedral coordination sphere of the metal. Our previous solid state and solution studies established an anticlinal J=P-Co-Cp metallophosphonate M-P rotamer preference both in hydrogen bonded [12,21,22,26,28] and non-hydrogen bonded [25] (Fig. 4: A, $L = PR_3$) examples. The solid state structure of complex 7bß adopts an unusual synclinal O=P-Co-Cp' conformation (Fig. 4: C; $Cp'=C_sMe_s$, R,R' = OMe) observed previously only for the Schiff base analogs [19] and for $(\eta^{5}-C_{9}H_{7})Co(PPhMe_{2})(C_{3}F_{7})-(P(O)(Ph)-$ (OMe)) [25]. Our initial conformational analysis [25] for metallophosphonates and -phosphinates was based primarily on the steric model developed by Seeman and Davies [38,40] for pseudo-octahedral piano-stool molecules in which the least sterically demanding ligand, assumed to be the phosphoryl oxygen in our work, straddles the remaining two legs (Fig. 4: A). However, the emergence of the series 7 (see following discussion) and their Schiff base analogs [19] which are clear and patterned departures from steric predictions suggest that a more detailed analysis is merited and that stereoelectronic [39,42-44] and/or dipole [40] effects may play a significant role in determining torsional energy profiles for O=P-Co-Cp.

Solution NMR studies of 7 imply a significant population of the same rotamer (Fig. 4: C'; R,R' = OMe) found in the



solid state structure of $7b\beta$. Measurements on molecular mechanics models of $7b\beta$ constructed from crystallographic coordinates showed that, with P-OMe and PO-Me bond rotations as the only degrees of freedom, pyrrole H_3 and H_5 approach within 2.7 Å and H₄ within 3.2 Å of the synclinal (R-P-Co-N)POMe but are ~ 6.5 Å from the remaining anticlinal (R'-P-Co-N)POMe of rotamer C' (Fig. 4: C'; R,R' = OMe). Proton nOed experiments in CDCl₃ accordingly show enhancements of the H₃, H₄ and H₅ pyrrole signals on partial saturation of the high field but no enhancement on saturation of the low field $P(O)(OMe)_2$ doublet in $7a\beta$ and 7bB. The measured nOed effects are inconsistent with significant populations of rotamers A or B (Fig. 4: A', B'; R,R' = OMe). Models of A' with synclinal R'-P-Co-N and anticlinal R-P-Co-N (R'R = OMe) predict nOe enhancements between R' and H. Models of rotamer B' with synclinal R-P-Co-N and R'-P-Co-N (R,R' = OMe) predict nOe enhancements between R and H5 as well as between R' and all pyrrole ring hydrogen atoms.

Examination of the diastereotopic phosphonate chemical shift difference ($\Delta \delta_{OMe}$) supports this analysis. Table 6 and Fig. 5 summarize the ¹H NMR chemical shift difference ($\Delta \delta_{OMe} = \delta_{OMe} - \delta'_{OMe}$) for the diastereotopic P(O)-

(OMe), groups in the chiral dimethylphosphonate complexes. The dimethylphosphonate complexes can be divided into three groups with $\Delta \delta_{OMe}$ (Group I) $\gg \Delta \delta_{OMe}$ (Group II) $>\Delta \delta_{OMe}$ (Group III) according to their structure and magnitude of $\Delta \delta_{OMe}$. Group I consists of those complexes in which one methoxyl group of $P(O)(OMe)_2$ is positioned directly over the bidentate N,O- ligand (Fig. 4: B', C') as found in the solid state molecular structure of 7bß. A significant population of this conformation establishes an anisotropic methoxy environment due to differences in long range shielding derived from the ring current effect and results in large $\Delta \delta_{OMe}$ values (111–249 Hz). Group II contains complexes with intramolecular P=O···H bonding, which prevents rotation about the Co-P bond (Fig. 4: A) and thus populate essentially a single Co-P rotamer. As a result, the methoxyl groups sense a moderate anisotropic environment and have $\Delta \delta_{OMe}$ values in the range 15-45 Hz. Group III comprises complexes in which there is no added constraint in Co-P(=O) rotation and no obvious source of anisotropy hence the diastereotopic OMe groups sense a similar environment and have the smallest $\Delta \delta_{OMe}$ values. Note that almost all complexes in Group III have $\Delta \delta_{OMe}$ less than 6 Hz, except for $(\eta^5-C_5Me_5)Co(P(OMe)_3)(I)(P(O) (OMe)_2$) $(\Delta \delta_{OMe} = 12$ Hz, entry C2 of Table 6), $(\eta^5 - C_5 H_3 - 12 Hz)$ $(CHMe_2)_2)Co(PMe_3)(OCOCF_3)(P(O)(OMe)_2)(\Delta\delta_{OMe})$ = 9 Hz, entry C3 of Table 6) and $(\eta^5 - C_9 H_7) Co(PPhMe_2)$ - $(C_3F_7)(P(O)(OMe)_2)$ ($\Delta \delta_{OMe} = 18$ Hz, entry C1 of Table 6). Owing to the increased steric requirements of π^5 -C₅Me₅ and η^5 -C₅H₃(CHMe₂)₂ compared to η^5 -C₅H₅ and η^5 -C₉H₇ [45,46] and PPhMe₂ [47,48] compared to the remaining phosphines in group C, the Co-P(O)(OMe)₂ rotamer populations are more skewed.

Molecular mechanics [40] (MM+ force field) and extended Hückel [38-41] (EHMO) studies were carried out on analogs of 7 to determine energy profiles [38] for metallophosphonate O=P-Co-Cp torsion. It is well known that the frontier donor orbitals of chiral CpMLL' fragments which control conformation of π -bonded ligands critically depend on the relative donor/acceptor properties of the ligands L and L' [43,49]. Transfer of available literature data describing ligand sets L, L' = CO, NO [49], PH₃, CO [49] and NO, PH₃ [44] to the bidentate N,O ligand 2 examined in this study was not straightforward hence an EHMO study was carried out. Fragment molecular orbital (FMO) analysis of an idealized structural model of 7 ($(\eta^5-C_5H_5)Co(HC(O)-$ C4H3N)(P(O)H2)) intended to identify possible stereoelectronic factors manifested by preferential HOMOmetal/ LUMO_{phosphonate} alignment [49] revealed a manifold of π interactions with orbitals of varying metal character hence only the total energies are presented. It is interesting to note in this context that EHMO calculations of carbene torsion in the model complex $[(\eta^5-C_5H_5)Co(HC(O)-C_4H_3N) (CH_2)$]⁺, which were carried out to map preferred π -bonding orientations in the chiral organometallic fragment, detect a minimum energy conformation showing the carbene plane aligned with the Co-O rather than the Co-N bond.

Table 6

Comparison of the 'H NMR diastereotopic chemical shift differences for metallophosphonates; (P(O)(OMe)₂)

Group	No.	Metallophosphonate		δοΜα	δ' _{OMe}	$\Delta \delta_{OMe}^{a}$		Ref.
		L_n -Co-P(O)(OMe) ₂		(ppm)	(ppm)	(ppm)	(Hz)	
[Al	7εα		3.66	2.97	0.69	207	b
	A2	7aβ		3.65	2.93	0.72	216	b
	A3	76α		3.59	2.76	0.83	249	ь
	A4	7Ъβ		3.54	2.77	0.77	231	b
	A5a	η ⁵ -C ₅ H ₅ , N-N* °	S _{Co}	3.44	3.07	0.37	111	d
	A5b		R _{Co}	3.42	2.99	0.43	129	
II	Bla	η ⁵ -C ₅ H ₅ , PNH °, I	S _{Cu}	3.82	3.68	0.14	42	f
	Blb		R _{Co}	3.83	3.66	0.17	51	
	B2a	η^{5} -C ₅ Me ₅ , PNH, I	Sco	3.79	3.70	0.09	27	g
	B2b		R _{Co}	3.77	3.64	0.13	39	
	B3a	η^5 -C ₅ H ₅ , PNH, C ₃ F ₇	R _{Co}	3.84	3.77	0.07	21	h
	B3b		S _{Co}	3.83	3.77	0.06	18	
	B4a	η^5 -C ₅ H ₅ , PNH, CF ₃	R _{Co}	3.82	3.77	0.05	15	h
	B4b		S _{Co}	3.82	3.77	0.05	15	
	B5a	η ⁵ -C ₉ H ₇ , PNH, C ₃ F ₇	R _{Co}	3.81	3.69	0.12	36	j
	B5b		S _{Co}	3.80	3.67	0.13	39	
	B6a	η^5 -C ₅ H ₅ , PEtNH ¹ , C ₃ F ₇	R _{co}	3.75	3.60	0.15	45	j
	B6b		S _{Co}	3.76	3.68	0.08	24	
	B7a	η^{5} -C ₉ H ₇ , PEtNH, C ₃ F ₇	R _{Co}	3.75	3.54	0.21	63	j
	В7ь		Sc.	3.76	3.66	0.10	30	
	B8a	η^5 -C ₅ H ₅ , PEtNH, I	S _{Co}	3.83	3.72	0.11	33	j
	B8b		R _{Co}	3.84	3.72	0.12	36	
	B9a	η^5 -C ₅ Me ₅ , PEtNH, I	S _{Co}	3.76	3.70	0.06	18	j
	B9b		R _{Co}	3.77	3.69	0.08	24	
m	CI	η^5 ·C ₉ H ₇ , PPhMe ₂ , C ₃ F ₇		3.77	3.71	0.06	18	k
	C2	$\eta^5 \cdot C_5 Me_5$, P(OMe) ₃ , I		3.68	3.64	0.04	12	j
	C3	η^5 -C ₅ H ₃ (CHMe ₂) ₂ , PMe ₃ , OCOCF ₃		3.63	3.60	0.03	9	1
	C4	η^5 -C ₅ H ₅ , P(OMe) ₃ , I		3.75	3.74	0.01	3	j
	CS	η^5 -C ₅ H ₅ , P(OMe) ₃ , PMe ₃		3.72	3.70	0.02	6	1
	C6	π^{5} -C ₅ H ₅ , P(OMe) ₃ , C ₃ F ₇		3.67	3.66	0.01	3	k
	C7	η^{5} -C ₅ H ₅ , PMe ₃ , C ₃ F ₇		3.67	3.66	0.01	3	k
	C8	η^{5} -C ₉ H ₇ , (POMe) ₃ , C ₃ F ₇		3.65	3.64	0.01	3	k
	C9	η^{5} -C ₉ H ₇ , P(OMe) ₃ , C ₆ F ₁₃		3.66	3.64	0.02	6	k
	C10	η^{5} -C ₉ H ₇ , PMe ₃ , C ₃ F ₇		3.65	3.63	0.02	6	k

* $\Delta \delta_{OMe} = S_{OMe} - \delta'_{OMe}$, operating frequency 300.1 MHz.

^b This work.

- ^c N-N^{*} = (S)-C₄H₃N-C=N-CH(Me)Ph.
- ^d Ref. [19].
- ^c $PNH = (S)-PPh_2-NH-CH(Me)Ph.$
- ' Ref. [21].
- 8 Ref. [28].
- h Ref. [26].
- $PEtNH = (S)-PEt_2-NH-CH(Me)Ph.$
- ⁱ Ref. [66].

¹ Ref. [67].

Whether the bonding of the chiral fragment $[(\eta^5-C_5H_5)C_0(R'C(0)-C_4H_3N)]^+$ to $P(O)(OR)(R)^-$ will be conformationally sensitive is determined by the nature of its π -type orbitals and their interaction with the appropriate metal π -orbitals. We can expect that stereoelectronic considerations for the $C_{2\nu}$ [P(O)(OMe)₂]⁻¹ fragment will be less clear cut that for a single faced π -acceptor ligand [50]. Current interpretations [51-54] identify the much discussed

 π -bonding ability of phosphorus $C_{3\nu}$ PX₃ ligands with stabilizing 2e⁻ interactions between filled, metal centered π orbitals and empty P-X σ^* -orbitals of π symmetry derived from d-function polarized phosphorus p-valence orbitals. Destabilizing, 4e⁻ interactions with filled π -type PX₃ orbitals can also be expected to play a role as they do in determining the conformation L_n[M]-Me complexes [55]. Our low level extended Hückel calculations for the $C_{2\nu}$

^{*} Ref. [25].



Fig. 5. ¹H NMR chemical shift difference for diastereotopic P(O)(OMe)₂ groups in the chiral dimethylphosphonate complexes.

 $[P(O)(OMe)_2]^{-1}$ fragment find no appreciable difference in calculated torsional energies with and without the inclusion of phosphorus d-orbitals. However, in the absence of phosphorus d-orbitals PX₃ σ^* energies were very high and did not appreciably contribute to occupied π -type MOs. Examination of MO energies as a function of torsional angle at the Hückel level showed that no single orbital dominates and that the total torsional energy is the sum of :nany small contributions.

Fig. 6 compares the total relative EHMO and MM+ energy profiles for O=P-Co-Cp torsion determined for several related compounds. EHMO calculations of 7bß, 7aß and the model structure $(\eta^5 - C_5 H_5)Co(HC(O) - C_4 H_3 N)$ -(P(O)H₂) were based on unoptimized, solid state geometries. Molecular mechanics calculations for $7b\beta$ proceeded from MM + optimized crystal coordinates. Viewed with the P atom in front, positive O=P-Co-N torsion designates clockwise rotation. As pointed out by Seeman and Davies [38] these pseudo-octahedral piano-stool structures cannot achieve perfectly staggered or eclipsed conformations. Nevertheless, both EHMO and MM + calculations detect a threefold rotational barrier with O=P-Co-N torsion minima at ~40, 150-175 and 275° corresponding to approximately staggered conformations A. B and C of Fig. 4. Calculated O=P-Co-N torsional barriers for the C5H5 complexes are in the range 10-20 kJ mol⁻¹, however much larger barriers were evident for the C_5Me_5 analog $7b\beta$.

Some discrepancy exists between the results obtained from the extended Hückel and MM + algorithms. Not unexpectedly the MM + calculations for **7b** β concur with predictions based on the Seeman–Davies steric model and predict an *anticlinal* O=P-Co-Cp low energy rotamer with the smallest (oxo) group straddling the bidentate N,O legs (Fig. 4: $E_{A'} < E_{B'} \approx E_{C'}$). EHMO calculations for **7b** β (Fig. 4: $E_{C'} < E_{A'} \approx E_{B'}$), **7a** β and for the model structure (η^{5} -C₅H₃)Co(HC(O)-C₄H₃N)(P(O)H₂) (Fig. 4: E_{B'} < E_{A'}



Fig. 6. Comparison of EHMO and MM + energy profiles for O=P-Co-Cp torsion for several related compounds.

 $\approx E_{C'}$) predict an O=P-Co-Cp synclinal rotamer to be most stable. On balance, both MM and EHMO calculations fail to reliably rationalize the observed solid state conformation (Fig. 4: C'). We speculate that the incorrect predictions of both the MM + and extended Hückel calculations may be a result of dipolar effects which mitigate against rotamer C (Fig. 4).

2.7. Reaction of $(\eta^5 - C_5H_5)Co(R'C(O) - C_4H_3N)(1)$ with dimethyl phenylphosphonite

Reaction of $(\eta^5-C_5H_5)Co(R'C(O)-C_4H_3N)(I)$ (3aa, $3a\beta$) with prochiral PPh(OMe)₂ proceeded readily at room temperature to give a mixture of diastereomeric phosphinate products, $(\eta^5-C_5H_5)Co(R'C(0)-C_4H_3N)(P(0)-$ Ph(OMe)) (8aα-1,2 and 8aβ-1,2, respectively). Metallophosphinate formation proceeds via initial iodide substitution to give cationic intermediates $(\eta^5 \cdot C_5 H_5) Co(R'C(O) C_4H_3N$ (PPh(OMe)₂)]⁺ (**6a** α , **6a** β), which were detected by proton NMR in acetone-d₆ at room temperature (Scheme 1) (6aa, Cp: 5.94 ppm, PPh(OMe)₂: 4.02 ppm (d, 11.5 Hz), 3.94 ppm (d, 11.0 Hz); 6a, Cp: 5.96 ppm, PPh(OMe)₂: 4.04 ppm (d, 11.9 Hz), 3.96 ppm (d, 11.5 Hz)). Deep red cation $6a\beta$ was precipitated by the rapid addition of excess PPh(OMe)₂ to a benzene solution of $3a\beta$ at room temperature. Subsequent nucleophilic attack of the displaced iodide at carbon occurs to afford the isolated metallophosphinates, 8a.

Reactions of PPh(OMe)₂ with the bulkier $(\eta^5-C_5H_5)-Co(R'C(O)-C_4H_3N)(I)$ (3b α , 3b β) were very slow compared to the cyclopentadienyl substrates and extended reflux

in benzene was necessary to obtain the corresponding pentamethylcyclopentadienyl phosphinates, $(\eta^5-C_5Me_5)Co(R'C-(O)-C_4H_3N)(P(O)Ph(OMe)$ (**8ba-1,2; 8b\beta-1,2**). Chiral induction from Co^{*} \rightarrow P was very low (0–14%) compared to other systems studied [12–19,21,22,25], possibly because of reduced asymmetry in the coordination sphere.

Chromatographic separation of diastereomers from the reactions of $(\eta^5 - C_5 R_5) Co(R'(C(O) - C_4 H_3 N)(I))$ (3a α , $3a\beta$, $3b\alpha$ or $3b\beta$) and PPh(OMe)₂ was unsuccessful. These diastereomers can, however, be distinguished by NMR spectroscopy. Complexes 8aa-1,2, 8aB-1,2, 8ba-1,2 and 8bB-1.2 were characterized by IR and NMR as diastereomeric mixtures. The methyl phenylphosphinates show ν (C=O) and ν (P=O) (Table 1) in the ranges 1546–1564 and 1135-1144 cm^{-'}, respectively. ¹H NMR spectra (Table 2) of the diastereomeric product mixtures were assigned using ¹H nOed spectra and confirmed by comparison with the spectra of other phosphinates [19,25]. 'H NMR in the Cp/Cp* and pyrrolyl regions were similar to their reaction precursors ($3a\alpha$, $3b\beta$) and the related dimethyl phosphonate complexes (7aa, 7bB). All methyl phenylphosphinate complexes showed a characteristic doublet assigned to the methoxyl group P(O)Ph(OMe) in the range 3.3-3.8 ppm $({}^{3}J(PH) = 11.0 \pm 0.5)$. The ${}^{13}C$ NMR spectra tabulated in Table 3 and assigned on the basis of 2-D ¹H/¹³C ¹J heterocorrelation spectra show characteristic resonances for η^5 -Cp/Cp* piano-stool metallophosphinates [19,25].

3. Experimental

3.1. Reagents and methods

Although the Co(III) products are air stable in the solid state and in solution, reactions were carried out under an atmosphere of dry nitrogen. Benzene, hexane, pentane and THF solvents were distilled from a blue solution of benzophenone ketyl. Methylene chloride was distilled under nitrogen from $P_4O_{10}(s)$, acetone from activate 4A sieves (4-8 mesh), and methanol from NaOMe, respectively. NaH (95%), 2-formylpyrrole (HC(O)-C₄H₃NH) and 2-acetylpyrrole (Me-C(O)-C4H3NH) were purchased from Aldrich and used as received. Qualitative thin layer chromatographic analyses were performed using Merck precoated (silica gel F-254) plates. Preparative chromatographic separations were carried out using a Chromatotron (Harrison Associates) with 1, 2 or 4 mm thick silica gel 60 (Merck, 230-400 mesh). Elemental analyses were performed by Canadian Microanalytical Service Ltd. (Delta, BC). Melting points were measured in sealed, nitrogen filled capillaries and are uncorrected. IR spectra were recorded as thin films on a Mattson Polaris instrument with 4 cm⁻¹ resolution. NMR spectra were measured on a GE 300-NB instrument operating with a proton frequency of 300.12 MHz. Proton nOed spectra were determined under steady state conditions as described previously [21]. Complexes (η^{5} -C₅R₅)Co(CO)(I)₂(R = H, Me) were prepared using the established procedures [56,57].

3.2. Crystal structure determination of $(\eta^5 - C_5 M e_5)Co$ -($Me - C(O) - C_4 H_3 N)(Y) (Y = I (3b\beta), P(O)(OMe)_2 (7b\beta))$

Crystal data were collected at ambient temperature on a Rigaku AFC6S diffractometer using graphite monochromated Mo K α radiation. Weak reflections ($I < 10.0\sigma(I)$) were rescanned (max. 2) and the counts accumulated to assure good counting statistics. The structure of 7bB was solved by direct methods [58,59]. Neutral atom scattering factors were taken from Cromer and Waber [60]. Anomalous dispersion effects were included in F_{ealc} [61] and the values for $\Delta F'$ and $\Delta F''$ were those of Cromer [62]. All calculations were performed using the TEXSAN [63] crystallographic software package of the Molecular Structure Corporation. The space group $P2_1/c$ (No. 14) for **7b** β was assigned on the basis of systematic absence (h0l: $l \neq 2n$ and 0k0: $k \neq 2n$) and on the successful solution and refinement of structure. Solution and refinement of $3b\beta$ was complicated by rotational disorder of the C5Me5 group which was modeled as two coually contributing structures with all rings introduced as rigid groups. Further complications resulting from a second type of disorder which enabled both enantiomers to occupy the same position in the cell were encountered (see text). Although the diffraction data for $3b\beta$ were refined, an unreasonable C(14)-C(15) bond distance resulted hence structural data are not reported. Selected bond distance/bond angle data and atomic coordinates for $7b\beta$ are listed in Tables 4 and 5. PLUTO diagrams of the molecular structures obtained for 3bß and 7bß are shown in Figs. 1 and 3. Further crystal parameters are given in Table 7.

3.3. Molecular mechanics and extended Hückel calculations

MM+ calculations were carried out using the standard MM + force field of HyperChem (Release 4). Starting structures for minimization were obtained from crystal coordinates or using the HyperChem draw interface. Structures were minimized (Polak Ribiere optimization) to convergence following rotation about the O=P--Co--Cp torsion and the optimized result was used to spawn the next rotamer. The initial structure had an O=P-Co-Cp torsional angle of +145°. Extended Hückel calculations were carried out using CACAO (Version 4.0) [64]. Internal coordinates for input to the CACAO programme were calculated from X-ray data for 7bB. A Hückel parameter of 1.75 was used throughout. Orbital exponents were those supplied with CACAO [64]. Phosphorus valence orbital parameters $(H_{ii} (\zeta_1), 3s = -18.60 \text{ eV} (1.6),$ 3p = -14.00 eV (1.6), 3d = -7.0 eV (1.4), were taken from the literature [65].

Table 7		
Summa	ry of crystallographic data	for 7bβ

	Τъβ
Formula	C::#H27NO4PC0
FW (g mol ⁻¹)	411.32
Crystal habit	deep-red prism
Crystal size (mm)	0.40×0.30×0.10
Crystal system	monoclinic
No. reflections used for unit cell determination (2θ range)	25 (40.3-45.2°)
Omega scan peak width at half-height	0.33
Lattice parameters	
a (Å)	12.183(1)
<i>b</i> (Å)	10.100(2)
c (Å)	16.915(2)
β(°)	106.559(9)
$V(\dot{A}^3)$	1995,1(4)
Space group	P_{2_1}/c (No. 14)
Z	4
$D_{\text{calc}}(\text{g cm}^{-3})$	1.369
F(000)	864
$\mu(Mo K\alpha) (cm^{-1})$	9.56
Scan width (°)	1.10 + 0.30 tan <i>θ</i>
2θ _{mm} (°)	50.0
No. reflections measured	
Total	3911
Unique	3729
Rine	0.022
Corrections *	Lorentz-polarization absorption
transmission factors	0.85-1.00
secondary extinction coefficient	
Function minimized	$\sum w(F_{e} - F_{e})^{2}$
Least-squares weights	$4F_{c}^{2}/\sigma^{2}(F_{c}^{2})$
p Factor	0.01
Anomalous dispersion	all non-hydrogen atoms
No. observations $(I > 3.00\sigma(I))$	2716
No. variables	226
Reflection/parameter ratio	12.02
Rb	0.036
R., °	0.039
Goodness of fit indicator ^d	2.31
Max. shift/error in final cycle	0.00
Max, peak in final difference map ($e Å^{-3}$)	0.30
Min. peak in final difference map ($e Å^{-3}$)	0.33

* See Ref.[68].

 ${}^{\rm b}R = \sum ||F_{\rm o}| - |F_{\rm c}||/\sum |F_{\rm o}|.$

 ${}^{c}R_{w} = [(\Sigma w(|F_{o}| - |F_{c}|)^{2} / \Sigma w F_{o}^{2})]^{1/2}.$

^d GOF = $(\sum (|F_0| - |F_c|)/\sigma)/(n-m)$ where n = no. of reflections, m = no. of variables, and $\sigma^2 = variance$ of $(|F_0| - |F_c|)$.

3.4. Synthesis of $(\eta^5 - C_5 R_5) Co(R' - C(O) - C_4 H_3 N)(I)$ (3a α -3b β)

As summarized in Table 8, the preparation of complexes $3a\alpha-3b\beta$ followed a similar procedure. The preparation of $3a\alpha$ is exemplary. Excess NaH was added to 100 ml of THF solution of 2-formylpyrrole (2α H, 174.6 mg, 1.836 mmol) with stirring at room temperature. After evolution of hydrogen gas ceased, the reaction was stirred for about 60 min. The solution was filtered through a glass frit fitted with a 2 cm plug of Celite and washed with THF (3×20 ml). The combined filtrate and washings (2α) were dropped into 100 ml

of THF solution of $(\eta^5 \cdot C_5 H_5)Co(CO)(I)_2$ (1a, 731.7 mg, 1.803 mmol) with stirring at room temperature by means of a pressure equivalent dropping funnel over a 20 min period. The solution color changed from purple to blue. After stirring for an additional 1 h the solvent was removed at aspirator vacuum. The resulting blue sticky residue was extracted with 50 ml of dichloromethane and passed through a glass frit fitted with a 10 cm silica gel (230-400 mesh) plug. Evaporation of the solvent left the crude product, which was purified by radial thick layer chromatography. The product was obtained as the first blue band on elution with dichloromethane/benzene (4/1, vol./vol.). Removal of the solvent from

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Зас	н	н	-	1a, 0.732 g (1.80 mmol) 2aH, 0.175 g (1.84 mmol)	THF (260 nl)	22	1.5	10 cm silica gel column (CH ₂ CI ₂) followed by radial plate chromatography (CH ₂ CI ₂ /benzene, 4/1)	0.448 g (72%)
3aβ	н	Me	-	1a, 1.064 g (2.623 mmol) 2βH, 0.291 g (2.66 mmol)	THF (300 ml)	22	1.0	10 cm silica gel column (CH2Cl2)	0.734 g (78%)
3ba	Me	н	Ι	1b, 1.175 g (2.468 mmol) 2œH, 0.240 (2.52 mmol)	THF (200 ml)	52	0.5	10 cm silica gel column (CH ₂ Cl ₂)	0.666 g (65%)
3b <i>β</i>	Me	Me	1	1b, 1.025 g (2.154 mmol) 2 βH , 0.243 g (2.23 mmol)	THF (250 ml)	22	0.5	10 cm silica gel column (CH ₂ Cl ₂)	0.691 g (75%)
4aß	н	Me	PMe ₃	3a <i>f</i> , 0.052 g (0.14 mmol) PMe ₃ , 0.015 g (0.20 mmol)	benzene (15 ml)	22	0.2	filter, wash with benzene $(3 \times 5 \text{ ml})$ and pentane $(3 \times 5 \text{ ml})$	0.059 g (95%)
4ba	Me	H	PMe ₃	3ba , 0.066 g (0.16 mmol) PMe ₃ , 0.030 g (0.40 mmol)	benzene (15 ml)	22	10	filter, wash with benzene $(3 \times 5 \text{ ml})$ and pentane $(3 \times 5 \text{ ml})$	0.067 g (86%)
4b <i>β</i>	Me	Me	PMe ₃	3bβ , 0.070 g (0.16 mmol) PMe ₃ , 0.100 g (1.31 mmol)	benzene (15 ml)	22	0.5	remove volatiles/high vacuum	0.082 g (99%)
6aβ	н	Me	PPh(OMe) ₂	3aß , 0.156 g (0.44 mmol) PPh(OMe) ₂ , 0.096 g (0.56 mmol)	benzene (15 ml)	22	0.2	filter wash with benzene $(5 \times 5 \text{ ml})$ and pentane $(5 \times 5 \text{ ml})$	0.160 g (70%)
7a.r	н	Н	P(O)(OMe) ₂	3ao , 0.040 g (0.12 mmol) P(OMe) ₃ , 0.024 g (0.20 mmol)	benzene (15 ml)	22	15	radial plate chromatography (acetone followed by methanol	0.023 g (60%)
7aβ	I	Me	P(O)(OMe) ₂	3aß, 0.358 g (0.999 mmol) P(OMe) ₃ , 0.224 g (1.81 mmol)	benzene (30 ml)	22	15	radial plate chromatography (acetone followed by acetone/ methanol (10/1))	0.333 g (98%)
Tba	Me	H	P(O)(OMe) ₂	3bo r, 0.108 g (0.261 mmol) P(OMe) ₃ , 0.051 g (0.41 mmol)	benzene (20 ml)	80	3	radial plate chromatography (acetone followed by methanol)	0.098 g (94%)
Tbβ	Me	Me	P(O)(OMe) ₂	3bβ , 0.113 g (0.264 mmoi) P(OMe) ₃ , 0.048 g (0.39 mmol)	benzene (20 ml)	80	9	radial plate chromatography (acetone followed by methanol)	0.101 g (93%)
8aa	H	н	P(O)Ph(OMe)	3a α, 0.045 g (0.13 mmol) PPh(OMe) ₂ , 0.035 g (0.21 mmol)	benzene (20 ml)	22	5.5	radial plate chromatography (acetone/methanol (25/3))	0.034 g (71%) 1/2=57/43
βaβ	H	Me	P(O)Ph(OMe)	3a ß. 0.154 g (0.428 mmol) PPh(OMe) ₂ , 0.087 g (0.51 mmol)	benzene/ CH ₂ Cl ₂ (30/10 ml)	22	15	remove volatiles/high vacuum	0.158 g (95%) 1/2=53/47
8ba	Me	н	P(O)Ph(OMe)	3b α, 0.072 g (0.17 mmol) PPh(OMe) ₂ , 0.065 g (0.38 mmol)	benzene (20 ml)	80	15	radial plate chromatography (acetone/methanol (20/1))	0.071 g (92%) 1/2=51/49
βþβ	Me	Me	P(O)Ph(OMe)	3b, 0.074 g (0.17 mmol) PPh(OMe) ₂ , 0.065 g (0.38 mmol)	benzene (20 ml)	80	15	radial plate chromatography (acetone/methanol (20/1))	0.079 g (99%) 1/2=50/50

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the first blue band left a dark blue crystalline solid (447.9 mg, 72%). Slow diffusion of hexane into a dichloromethane solution of $3b\beta$ afforded dark blue prisms.

3.5. Synthesis of $[(\eta^{5}-C_{5}R_{5})Co(R'-C(O)-C_{4}H_{3}N)-(PMe_{3})]^{+}I^{-}(4a\beta-4b\beta)$

Complexes $4a\beta-4b\beta$ were prepared following the same general procedure as described for $4a\beta$ (see Table 8). PMe₃ (14.9 mg, 0.196 mmol) was added via syringe to 15 ml of benzene solution of $3a\beta$ (50.8 mg, 0.141 mmol) with stirring at room temperature. A deep red precipitate formed leaving a clear colorless solution. The precipitate was collected on a glass frit and washed with benzene (3×5 ml) and then pentane (3×5 ml). The product was dried in air for several hours to give a deep red powder (58.5 mg, 95%).

3.6. Synthesis of $[(\eta^{5}-C_{5}H_{5})Co(Me-C(O)-C_{4}H_{3}N)-(PPh(OMe)_{2})]^{+}I^{-}$ (66), an Arbuzov reaction intermediate

Excess PPh(OMe)₂ (96.0 mg, 0.564 mmol) was added quickly via syringe to 15 ml of benzene solution of $3a\beta$ (156.1 mg, 0.435 mmol) with stirring at room temperature. After stirring for about 10 min the solution color changed from blue to deep red and some deep red precipitate formed. The precipitate was collected on a glass frit and washed with benzene (5×5 ml) and then pentane (5×5 ml). After drying in air for several hours a deep red powder was obtained (159.9 mg, 70%).

3.7. Synthesis of $(\pi^{5} \cdot C_{5}R_{5})Co(R' - C(O) - C_{4}H_{3}N) \cdot (P(O)(OMe)_{2}) (7a\alpha - 7b\beta)$

The synthesis for complex $7a\beta$ is representative. Details of the reaction conditions for other complexes are given in Table 8. Excess P(OMe)₃ (224.0 mg, 1.805 mmol) was added to a 30 ml benzene solution of $3a\beta$ (358.3 mg, 0.9979 mmol) via syringe with stirring at room temperature. After stirring overnight volatiles were removed from the red solution at water aspirator pressure to leave a red sticky product. The crude product was purified by radial thick layer chromatography. Initial acetone elution removed a high R_f yellow band. Continued elution with acetone/methanol (10/1, vol./ vol.) separated the product as a red band. Removal of the solvent at water aspirator and then oil pump vacuum afforded a red solid (333.2 mg, 98%). Slow diffusion of hexane into a chloroform solution of $7b\beta$ at room temperature afforded deep red prisms suitable for X-ray structure determination.

3.8. Synthesis of $(\pi^{5}-C_{5}R_{5})Co(R'-C(O)-C_{4}H_{3}N)-(P(O)Ph(OMe))$ (8a α -8b β)

The synthesis of **8b** α is typical. Similar procedures were used for complexes **8a** α -**8b** β (see Table 8). Excess PPh(OMe)₂ (65.0 mg, 0.382 mmol) was added to 20 ml of benzene solution of **3b** α (72.0 mg, 0.173 mmol) via syringe with stirring at room temperature. Overnight reflux resulted in a color change from blue to red. TLC analysis showed that the reaction was complete and the two diastereomers (distinguishable by NMR) could not be separated. Removal of volatiles at water aspirator pressure left a sticky residue which was chromatographed on a radial thick layer plate eluting with acetone/methanol (20/1, vol./vol.). Removal of solvent from the first red band left a red solid (70.7 mg, 92%) containing a mixture of two diastereomers.

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