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RHODIUM(I) COMPLEXES OF FERROCENYLPHOSPHINES AS EFFICIENT ASYMMETRIC CATALYSTS. THE STRUCTURE OF $Fe(\eta^5\text{-}C_5H_3(P(CMe_3)_2\text{-}1,3)(\eta^5\text{-}C_5H_3(CHMeNMe_2)P(CMe_3)_2\text{-}1,2)$ *

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Summary

Rhodium(I) complexes of the chiral ligands $Fe(\eta^5\text{-}C_5H_{(5\text{-}n)}(P(CMe_3)_2)_n\text{-}1,3)(\eta^5\text{-}C_5H_3(CHMeNMe_2)P(CMe_3)_2\text{-}1,2$ ($n = 0$–2) are P–N bound, and are asymmetric hydrogenation catalysts. The configuration of the product from prochiral olefins is controlled by the planar chirality of the ligand. The catalyst with $n = 2$ is the most efficient affording optical yields as good as those obtained from more conventional systems embodying PAr_2 donors.

Crystals of the ligand $n = 2$ are monoclinic, $P2_1$, a 11.448(4), b 44.667(7), c 8.669(3) Å, β 111.98(1)°, V 4111(2) Å^3, $Z = 4$ (2 molecules per asymmetric unit), D_x 1.114, D_m 1.129 g cm^{-3} (by flotation in aqueous KI), final $R = 0.069$ for 4799 observed reflections. The molecule is chiral, with an (S,S) configuration, and the two crystallographically independent molecules have almost identical geometries and conformations. The cyclopentadienyl rings are close to planar, deviate slightly from coplanarity, and are rotated by about 7° from an eclipsed conformation; the substituent P and C atoms are significantly displaced from the ring planes. Fe–C bond lengths average 2.044 and 2.092 Å to unsubstituted and substituted C atoms, respectively.

Introduction

In previous studies [1,2,3] we have shown that ferrocenylphosphines **3a** and **3b** afford cationic rhodium(I) complexes $[(P\text{–}N)RhNBD]ClO_4$ which are catalyst precursors (the symbol (P–N) is used to designate that both PR_2 and NMe_2 groups of **3**

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* Dedicated to Professor Jack Halpern on the occasion of his 60th birthday.

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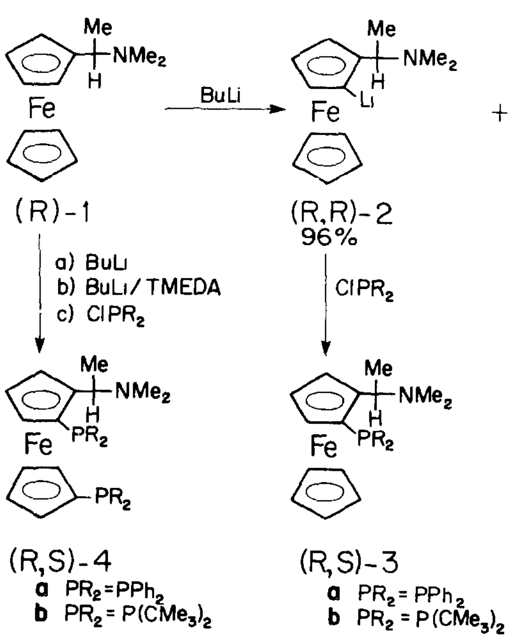
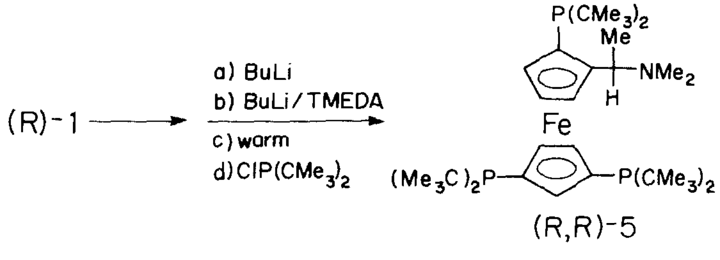
are bound to the rhodium [3]). These molecules **3** contain both a chiral carbon atom *CHMeNMe$_2$ and a plane of chirality and can be prepared as the (*R*,*S*)- or (*S*,*R*)-enantiomers (the first *R* (or *S*) designates the configuration at carbon; the second *S* (or *R*) the planar configuration). The compounds are easily prepared via the sequence shown in Scheme 1. The initial lithiation of the resolved amine **1** is highly stereo-specific [4] and the major diastereomer of **2** on treatment with ClPR$_2$ affords pure (*R*,*S*)-**3** or (*S*,*R*)-**3** [1,2]. The lithiation of **1** was likewise shown to afford **4a** [5].

SCHEME 1



The cationic rhodium(I) complexes of the chiral ligands **3a** and **4a** (Scheme 1) are effective catalysts for the asymmetric hydrogenation of acylaminoacrylic acid derivatives [1,6]. Unexpectedly the complexes of the dialkylphosphine **3b** proved to be more efficient catalysts than those of **3a** [2]. Thus it was of interest to prepare **4b** for comparison with **4a**.

We now report the synthesis of **4b** and the synthesis and crystal structure of the serendipitous product **5**, eq. 1, which was isolated as the unexpected diastereomer (*R*,*R*) or (*S*,*S*). The [(P–N)RhNBD]ClO$_4$ derivatives of **4b** and **5** are asymmetric catalysts for olefin hydrogenation, the latter providing exceptionally high optical yields.



(1)

Experimental

Unless otherwise specified air-sensitive reagents and products were manipulated in a nitrogen atmosphere using a double-manifold vacuum system and Schlenk techniques. All commercial chemicals were of reagent grade and were used as received unless otherwise stated. Solvents were purified and dried by standard techniques.

All liquid olefins were passed through a neutral Alumina column prior to use in hydrogenation reactions.

^1H NMR spectra were recorded on Bruker WP-80, Varian XL-100, or Bruker WH-400 spectrometers operating at 80 MHz, 100 MHz, or 400 MHz, respectively. ^1H shifts are reported relative to external TMS (δ 0 ppm) and ^{31}P shifts relative to 85% H_3PO_4, with $P(OMe)_3$ (δ +141.0 ppm) used as external standard. Infrared spectra were recorded on a Perkin–Elmer 598 spectrophotometer and mass spectra were obtained using a Kratos MS-50 instrument. Optical rotations were determined using a Perkin–Elmer model 241 MC polarimeter and CD spectra using a Jasco J-20 spectro-polarimeter. Microanalyses were performed by Mr. P. Borda of this department.

*Synthesis of (S,R)- and (R,S)-1,1′-bis(di-t-butylphosphino)-2′-(1-N,N-dimethylaminoethyl)ferrocene (**4b**)*

(*S*)-1-*N*,*N*-Dimethylaminoethylferrocene [4] (3 g, 11.7 mmol) was dissolved in a mixture of diethyl ether (2.5 ml) and n-hexane (3.5 ml) in a Schlenk tube. To this solution was added slowly n-BuLi (1.6 *M*, 8 ml) in hexane. The reaction was slightly exothermic and the color of the solution changed from yellowish brown to cherry red. The reaction mixture was stirred for 2 h, and a mixture of n-BuLi (1.6 *M*, 8 ml) in hexane and TMEDA (2 ml, 14 mmol) was added through a pressure equalizing dropping funnel. The reaction was slightly exothermic again, and the color of the solution deepened. The reaction mixture was further stirred for 6 h after which $(Me_3C)_2PCl$ [7] (4.1 g, 23 mmol) was added using a syringe. The reaction mixture was allowed to stir at room temperature for 2 days. Following hydrolysis with H_2O, the organic layer was separated, dried over $MgSO_4$, filtered, and reduced in volume to about 5 ml. The resulting red oil was chromatographed on neutral Alumina (Grade II) to give a single salmon-red band (eluted with diethyl ether/petroleum ether, 15/85). Removal of solvent under vacuum from the resulting orange solution afforded a dark orange oil (1.9 g, 30%). Attempted crystallization from acetone (or EtOH) was unsuccessful. (*R*,*S*)-**4b** was obtained by treating the (*R*)-aminoferrocene in the same manner as above.

Synthesis of (S,S)- and (R,R)-1,1′,3-tris(di-t-butylphosphino)-2′-(1-N,N-dimethylaminoethyl)ferrocene (5)

(*S*)-1-*N*,*N*-Dimethylaminoethylferrocene (3 g, 11.7 mmol) was dissolved in diethyl ether (5 ml) in a Schlenk tube. To this solution was added n-BuLi (1.6 *M*, 9 ml) in hexane. After stirring (2 h) a mixture of n-BuLi (1.6 *M*, 10 ml) in hexane and TMEDA (1.5 g, 13 mmol) was added dropwise through a pressure equalizing dropping funnel. The reaction mixture was further stirred for 15 h at room temperature. This solution was added dropwise to a solution of $(Me_3C)_2PCl$ (4.7 g, 26 mmol) in diethyl ether (30 ml) which was prepared in a 250 ml, round-bottom, three-necked flask equipped with a condenser, a N_2 inlet, and a pressure equalizing dropping funnel. After the initial exothermic reaction had ceased, the mixture was allowed to reflux for 20 h. Following hydrolysis with water, the organic layer was separated, dried over $MgSO_4$, filtered, and reduced in volume to about 5 ml. The resulting oily solution was chromatographed on Alumina (neutral, Grade I). After removal of the white phosphine by-product by elution with petroleum ether, a second salmon-red band was eluted with a mixture of diethyl ether and petroleum ether (1/9). Removal of solvents from the resulting orange solution afforded a dark oil which crystallized on adding acetone (or ethanol) to give the product (*S*,*S*)-**5** (0.32 g, 4%). (*R*,*R*)-**5** was obtained in the same manner.

Synthesis of ferrocenylphosphinerhodium(I) complexes

The complexes of the type [Rh(P–N)(NBD)]ClO_4, ((P–N) = **4b**, **5**) were prepared essentially using the procedure of Schrock and Osborn [8] with minor modifications, and were isolated as deep red crystals.

Hydrogenation studies

Hydrogenation reactions were carried out using a gas-uptake apparatus as described by James and Rempel [9]. The reaction conditions are given in Table 5. The products were worked up as follows: Acrylic acid derivatives, after the solvent was pumped off the residue was washed with cold dichloromethane (~ 5 ml) to leave the pure colorless product. Itaconic acid and α-methylcinnamic acids, after the solvent was removed the residue was dissolved in 25 ml of 5% NaOH, stirred, and filtered through Celite. The pale yellow filtrate was acidified (10% HCl) and extracted with diethyl ether (3 × 10 ml). The ether extract was dried ($MgSO_4$) and filtered, and the product was isolated following solvent evaporation.

X-Ray analysis of 5

A crystal of **5** with dimensions 0.3 × 0.2 × 0.2 mm was mounted in a general orientation on an Enraf–Nonius CAD4-F diffractometer. Unit-cell parameters were refined by least-squares on sinθ values for 25 reflections with $2\theta = 24$–$30°$ (Mo-K_{α_1} radiation, λ 0.70930 Å). Crystal data at 22°C are: $C_{38}H_{70}FeNP_3$ f.w. = 689.75. Monoclinic, $P2_1$, *a* 11.448(4), *b* 44.667(7), *c* 8.669(3) Å, β 111.98(1)°, *V* 4111(2) $Å^3$, $Z = 4$ (2 molecules per asymmetric unit), D_x 1.114, D_m 1.129 g cm^{-3} (flotation in aqueous KI), $F(000) = 1504$, μ(Mo-K_α) 5.05 cm^{-1}.

Intensities were measured with Mo-K_α radiation (graphite monochromator, λ 0.71073 Å) for reflections in the quadrant $hk \pm l$ with $0 < \theta < 26.0°$; ω scans were used, with ω scan angle $(0.90 + 0.35 \tan\theta)°$ (extended by 25% on each side for background counts), scan speeds 1.55–10.06° min^{-1}, and horizontal and vertical apertures of $(2.00 + \tan\theta)$ and 4 mm, respectively. Intensity check reflections were measured every hour (decrease of 3% over period of the data collection), and crystal orientation was checked after every 150 reflections. Intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied. Of 8145 reflections measured, 4799 (59%) had $I \geqslant 3\sigma(I)$, where $\sigma^2(I) = S + 2B + [0.07(S - B)]^2$, S = scan count, B = time-averaged background count.

Iron atom positions were determined from the Patterson map; these positions

TABLE 1

FINAL POSITIONAL (fractional $\times 10^4$, Fe and P$\times 10^5$) AND ISOTROPIC THERMAL PARAMETERS ($U \times 10^3$ Å^2) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z	U_{eq}/U_{iso}
Fe	−16807(15)	0	83(18)	36
Fe′	59384(14)	26219(4)	98954(19)	36
P(1)	−49562(27)	1715(7)	−23284(38)	41
P(2)	−1498(26)	6205(7)	26325(37)	38
P(3)	2325(33)	−6716(7)	21329(40)	49
P(1′)	88254(27)	24001(7)	131995(37)	38
P(2′)	40069(27)	19716(7)	82230(37)	38
P(3′)	35874(30)	32578(7)	87562(43)	47
C(1)	−3430(10)	215(2)	−612(14)	38(2)
C(2)	−2408(10)	425(2)	−306(14)	37(3)
C(3)	−1513(10)	395(2)	1352(13)	33(2)
C(4)	−1945(9)	157(2)	2068(13)	34(2)
C(5)	−3100(10)	37(3)	878(14)	42(3)
C(6)	−1826(12)	−237(3)	−2053(16)	55(3)
C(7)	−778(13)	−50(3)	−1572(17)	62(4)
C(8)	37(12)	−136(3)	67(16)	49(3)
C(9)	−502(10)	−375(2)	547(14)	38(2)
C(10)	−1674(11)	−440(3)	−734(15)	45(3)
C(11)	−2569(14)	−697(3)	−760(18)	66(4)
C(12)	−2254(19)	−977(5)	−1532(26)	105(6)
N	−3888(16)	−614(4)	−1395(21)	105(5)
C(13)	−4555(25)	−655(6)	−3226(34)	143(9)
C(14)	−4613(28)	−731(7)	−485(36)	157(10)
C(1.1)	−5969(12)	357(3)	−1289(16)	54(3)
C(1.2)	−6331(15)	99(3)	−332(19)	71(4)
C(1.3)	−7262(16)	469(4)	−2657(21)	78(4)
C(1.4)	−5347(14)	629(3)	−104(20)	71(4)
C(1.5)	−4911(12)	429(3)	−4072(15)	49(3)
C(1.6)	−3802(14)	305(3)	−4521(19)	68(4)
C(1.7)	−4788(14)	763(3)	−3749(19)	69(4)
C(1.8)	−6132(14)	369(3)	−5601(19)	70(4)
C(2.1)	234(12)	876(3)	1153(16)	53(3)
C(2.2)	1460(15)	1045(4)	2158(20)	74(4)
C(2.3)	−758(15)	1108(4)	172(20)	76(4)
C(2.4)	554(16)	665(4)	−67(22)	81(5)
C(2.5)	−910(11)	844(3)	3866(15)	46(3)
C(2.6)	−933(13)	627(3)	5256(18)	66(4)
C(2.7)	−2191(15)	971(4)	2897(19)	72(4)
C(2.8)	−8(14)	1106(3)	4793(19)	66(4)
C(3.1)	1816(15)	−723(4)	1875(20)	74(4)
C(3.2)	1456(17)	−769(4)	−19(22)	91(5)
C(3.3)	2332(19)	−1039(5)	2818(26)	105(6)
C(3.4)	2823(19)	−494(5)	2573(25)	102(6)
C(3.5)	513(12)	−507(3)	4274(16)	51(3)
C(3.6)	1408(16)	−710(4)	5612(21)	84(5)
C(3.7)	999(13)	−191(3)	4539(18)	64(4)
C(3.8)	−850(15)	−518(4)	4316(20)	75(4)
C(1′)	7174(10)	2357(2)	11761(13)	35(2)
C(2′)	6602(10)	2187(2)	10285(13)	33(2)
C(3′)	5259(10)	2178(2)	9802(13)	34(2)
C(4′)	5002(10)	2362(2)	11027(13)	37(2)
C(5′)	6156(10)	2470(2)	12182(13)	35(2)

TABLE 1 (continued)

Atom	x	y	z	U_{eq}/U_{iso}
C(6′)	7029(12)	2949(3)	9476(16)	50(3)
C(7′)	6398(11)	2791(3)	8001(15)	48(3)
C(8′)	5084(11)	2830(3)	7609(15)	51(3)
C(9′)	4924(10)	3016(2)	8871(13)	37(2)
C(10′)	6185(11)	3084(3)	10069(14)	41(3)
C(11′)	6444(13)	3297(3)	11512(18)	62(4)
C(12′)	6795(19)	3601(5)	11103(25)	100(6)
N′	7362(18)	3158(4)	13164(23)	114(5)
C(13′)	8608(24)	3225(6)	13440(32)	135(8)
C(14′)	7028(33)	3246(8)	14566(47)	196(14)
C(1.1′)	8817(12)	2112(3)	14824(15)	50(3)
C(1.2′)	8297(13)	2291(3)	16019(18)	64(4)
C(1.3′)	10169(14)	2005(3)	15890(18)	70(4)
C(1.4′)	8002(13)	1833(3)	14185(17)	58(3)
C(1.5′)	9847(12)	2255(3)	12077(15)	49(3)
C(1.6′)	9506(13)	2447(3)	10457(17)	58(3)
C(1.7′)	9701(14)	1912(3)	11570(18)	65(4)
C(1.8′)	11239(14)	2317(3)	13205(19)	69(4)
C(2.1′)	4720(13)	1804(3)	6778(17)	58(3)
C(2.2′)	3673(14)	1647(3)	5317(18)	66(4)
C(2.3′)	5849(15)	1577(3)	7504(19)	74(4)
C(2.4′)	5162(15)	2071(4)	6028(20)	78(4)
C(2.5′)	3773(12)	1655(3)	9579(16)	53(3)
C(2.6′)	2911(15)	1811(4)	10448(20)	73(4)
C(2.7′)	4910(15)	1528(4)	10883(20)	78(4)
C(2.8′)	2953(13)	1404(3)	8439(18)	61(4)
C(3.1′)	3009(14)	3399(3)	6486(19)	67(4)
C(3.2′)	4217(19)	3522(5)	6279(26)	102(6)
C(3.3′)	2155(17)	3670(4)	6430(23)	89(5)
C(3.4′)	2266(17)	3184(4)	5102(23)	94(5)
C(3.5′)	2370(13)	3006(3)	9087(17)	57(3)
C(3.6′)	1152(15)	3187(4)	8693(20)	77(4)
C(3.7′)	2131(15)	2702(4)	8143(20)	74(4)
C(3.8′)	2908(15)	2965(4)	10988(19)	72(4)

were confirmed and phosphorus positions determined by direct methods, the remaining non-hydrogen atoms then being located by Fourier methods. The structure was refined by full-matrix least-squares methods, with neutral atom scattering factors, anisotropic thermal parameters and anomalous scattering corrections for Fe and P, and non-methyl hydrogen atoms placed in calculated positions but excluded from the refinement. The function minimized was $\Sigma w(|F_0| - |F_c|)^2$, with $w = 1/\sigma^2(F)$, $\sigma^2(F)$ being derived from the previously defined $\sigma^2(I)$; for unobserved reflections $w = 0$. Convergence was reached at $R = 0.069$, $R_w = 0.094$ for the observed reflections (the opposite enantiomorph refined to $R = 0.071$, showing that the present results correspond to the correct absolute configuration); for all 8145 reflections $R = 0.116$. On the final cycle of refinement mean and maximum parameter shifts were 0.051 and 0.23 σ, mean error in an observation of unit weight is 2.18, and the final difference map had maximum fluctuations of $+0.68$ and -0.37 e Å^{-3}. Final

TABLE 2

SUMMARIZED BOND LENGTHS (Å) AND ANGLES (°) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Bond	1	2	
Fe–C(1)	2.102(11)	2.074(10)	
Fe–C(2)	2.050(11)	2.067(10)	
Fe–C(3)	2.083(10)	2.119(10)	
Fe–C(4)	2.044(10)	2.059(11)	
Fe–C(5)	2.038(11)	2.021(11)	
Fe–C(6)	2.029(13)	2.040(12)	
Fe–C(7)	2.013(14)	2.047(12)	
Fe–C(8)	2.041(13)	2.074(12)	
Fe–C(9)	2.092(11)	2.115(10)	
Fe–C(10)	2.069(12)	2.081(11)	
P(1)–C(1)	1.832(11)	1.844(11)	
P(2)–C(3)	1.841(10)	1.820(11)	
P(3)–C(9)	1.866(12)	1.844(11)	
P(1)–C(1.1)	1.903(13)	1.911(13)	
P(1)–C(1.5)	1.915(13)	1.894(13)	
P(2)–C(2.1)	1.886(13)	1.886(14)	
P(2)–C(2.5)	1.896(12)	1.919(13)	
P(3)–C(3.1)	1.922(16)	1.932(15)	
P(3)–C(3.5)	1.909(13)	1.895(14)	
			Mean
C–C (ring)	1.37–1.44(2)	1.39–1.46(2)	1.42
C–C (t-Bu)	1.49–1.63(2)	1.48–1.61(2)	1.55
N–C	1.44–1.49(3)	1.39–1.55(3)	1.46
C(11)–C	1.53, 1.52(2)	1.51, 1.50(2)	1.52
C–C–C (ring)	105.7–110.5(10)	105.0–111.3(10)	108.0
Angles at C(t-Bu)	101.7–119.3(10)	102.1–118.9(9)	109.4
C(ring)–P–C(t-Bu)	97.7–107.9(5)	98.1–106.9(5)	103.2
C(t-Bu)–P–C(t-Bu)	108.3–109.7(5)	108.0–110.9(6)	109.2
C–N–C	112–116(2)	111–112(2)	113

positional and thermal parameters are given in Table 1 *. Atomic scattering factors were from refs. 10 and 11, and anomalous dispersion corrections from ref. 12; computer programs used include locally written programs for data processing and locally modified versions of MULTAN80 [13], ORFLS [14], ORFFE [15], FORDAP [16], and ORTEP II [17]. A summary of bond lengths and angles is given in Table 2.

Results and discussion

The isolation of the bis-phosphine derivative **4b** proved to be more difficult than expected, most initial preparations being contaminated with the monophosphine **3b**. In attempts to force the lithiation reaction to go to completion excess BuLi and higher temperatures were employed; this resulted in the ultimate isolation of the

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* Lists of structure factors, calculated hydrogen atom positions, anisotropic thermal parameters, bond lengths and angles, torsion angles, and a packing diagram are available from the authors.

trisphosphine **5**. The reproducible procedures given in the experimental section afford yields of **4b** and **5** of 30 and 4%, respectively.

The analytical data for **4b** (as its rhodium(I) complex) and **5** indicate that they are formulated correctly. This is corroborated by their spectroscopic data particularly the ^{31}P NMR spectra which show the expected number of resonances. The crystal structure of **5** was determined to confirm the stereospecificity of the reactions producing it (Scheme 1; the anticipated configuration for both **4b** and **5** would be *S*,*R* starting from (*S*)-**1**).

Structure 5

The molecule of **5** (Fig. 1) is chiral, and the analysis has shown an *S* configuration for the amine-substituted C(11) atom, as expected, but an *S* configuration for the asymmetrically-substituted ferrocene moiety [4]. The structure contains two crystallographically independent molecules, which have almost identical geometries and conformations; the maximum differences are in the dimethylaminoethyl groups, which show torsion angle differences of up to 12(2)°.

Each iron atom is sandwiched between two cyclopentadienyl rings which are very close to planar, deviate slightly from coplanarity, and are separated by an average of 3.34 Å. The Cp(1) (C(1)–C(5)) and Cp(2) (C(6)–C(10)) rings are rotated by about 7° from an eclipsed conformation (an average of 8.5(12)° in molecule 1 (unprimed atoms) and 5.7(11)° in molecule 2 (primed atoms); rotation defined in terms of vectors from each Cp atom to the mean ring centre). The substituent groups on the upper and lower rings of each molecule are arranged in a staggered manner (Fig. 2). The detailed arrangement of the substituents is clear from Fig. 1; one noteworthy feature is that the nitrogen lone-pair is directed toward the Fe atom, although the mean Fe...N distance of 3.61 Å seems too long for any significant interaction. The angles between the ring planes are 3.9(10) and 4.9(10)° in the two molecules. The rings are almost exactly planar, with maximum displacement of the ring carbon atoms from the mean planes of 0.024(12) Å. The substituent atoms are however considerably displaced from the ring planes in directions away from the Fe atoms, P(1) and P(2) by an average of 0.24 Å (range 0.18–0.29 Å, individual σ 0.003 Å),

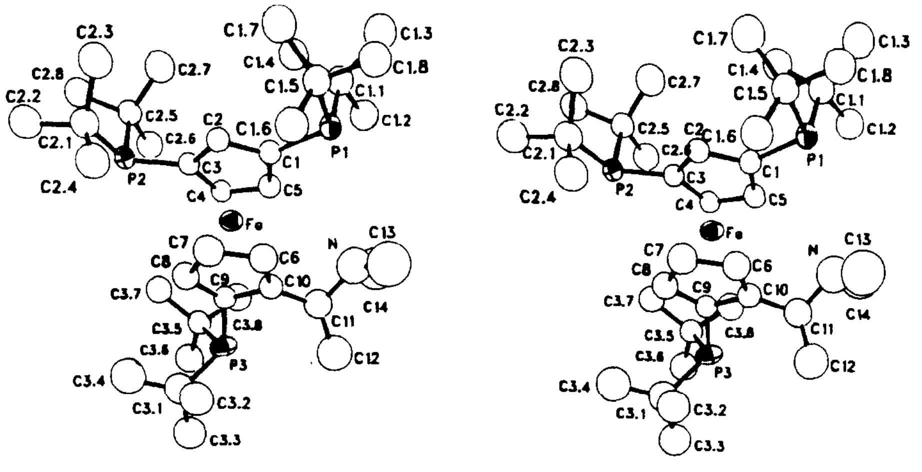


Fig. 1. Stereoview of 5, molecule 1, with 50% probability thermal ellipsoids; molecule 2 is almost identical.

P(3) by 0.58 Å (0.56 and 0.60 Å in the two molecules), and C(11) by 0.09 Å (0.06 and 0.12, σ 0.015 Å). These displacements probably result from steric repulsions between the substituent groups, the repulsions also probably being responsible for the small deviations from coplanarity of the two rings in the molecule (C(6) being closest to and P(3) furthest from the Cp(1) plane).

The Fe–C bonds (Table 2) fall into two distinct groups; those involving unsubstituted ring atoms are in the range 2.013–2.074(12), mean 2.044 Å, while for substituted atoms the distances are 2.069–2.119(11), mean 2.092 Å. The slightly longer average distances to the substituted carbon atoms suggest lower electron-density at these positions, particularly at those with phosphine substituents. These bond length variations probably cause the small deviations from ring planarity, the unsubstituted C atoms being displaced slightly toward the Fe atoms. The C–C bond lengths and C–C–C angles in the cyclopentadienyl rings also show some variations. Individual differences cannot be considered significant, but mean C–C lengths are 1.416 Å if the bond involves only unsubstituted C atoms and 1.426 Å if a substituted atom is involved; corresponding mean C–C–C angles are 109.0° at unsubstituted and 106.5° at subsituted C atoms. These variations again suggest lower electron-density at substituted carbon atoms.

The P–C(ring) bonds are 1.820–1.866(11), mean 1.841 Å, and P–C(t-Bu) are significantly longer at 1.886–1.932(15), mean 1.906 Å; the difference is in accord with the smaller σ-bond radius of C(sp^2) carbon atoms relative to C(sp^3), with perhaps some minor π-bond contribution in the P–C(ring) bonds. P atoms have a normal pyramidal geometry, with mean C(ring)–P–C(t-Bu) 103.2° and mean C(t-Bu)–P–C(t-Bu) 109.2°. Bond lengths and angles in the dimethylaminoethyl group are normal, mean C–C 1.52, C–N 1.47 Å, mean angle at C(11) and at N 113°.

As mentioned above the trisphosphine **5** is obtained under more forcing conditions than used for the preparation of **4b**. The isolated yield of **5** is low (4%) and reproducible but it is higher than that anticipated on the basis of Scheme 1 which would allow a maximum yield of 4%. This is because, for example, (*R*,*R*)-**5** would have to originate from (*R*,*S*)-**2**. It is our experience that the stereospecificity of the initial lithiation is lowered at higher temperatures [18]. This coupled with some redistribution of lithiated sites could lead to the isolation of **5**.

Because of this unexpected result it became necessary to check that the configuration of the other products was as expected. Kumada and coworkers [5] have established that the CD spectra of ferrocenylphosphines, such as **4a**, are dominated by contributions from the planar chirality. Positive Cotton effects are seen with maxima in the range 450–470 nm and negative ones in the range 340–350 nm if the configuration is *R*. This same pattern is seen in the CD spectra of (*S*,*R*)-**3b**,

(Continued on p. 16)

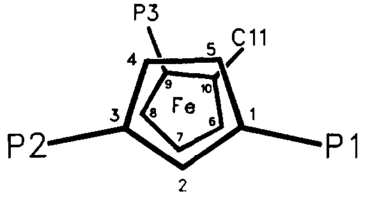


Fig. 2. View of **5** along the average normal to the cyclopentadienyl rings, showing the staggered arrangement of the substituents.

TABLE 3

ANALYTICAL AND SOME SPECTROSCOPIC RESULTS FOR CHIRAL LIGANDS AND COMPLEXES

Ligands, (P–N)	M.p. (°C)	$[\alpha]_D^a$	Analysis (Found (calcd.)(%))			^{31}P NMR ^{b}
			C	H	N	
(*S*,*R*)-**3b**	52– 55	+178.3°	41.02 (41.29)	5.57 (5.63)	2.23 (2.19)	13.32(s)
(*R*,*S*)-**3b**		−179.0°				
(*S*,*R*)-**4b**	oil	−22.2°	–	–	–	14.53(s), 26.74(s)
(*R*,*S*)-**4b**		+21.9°				
(*S*,*S*)-**5**	135–137	−37.5°	65.68 (66.10)	10.00 (10.29)	2.10 (2.03)	17.67(s), 23.49(s), 26.63(s)
(*R*,*R*)-**5**		+36.6°				
[(P–N)RhNBD]ClO$_4$, (P–N)						
(*S*,*R*)-**3b**		−72.3°	50.17 (50.12)	6.24 (6.19)	1.97 (2.01)	34.0 (bd, *J*(Rh–P) 154 Hz)
(*R*,*S*)-**3b**		+71.9°				
(*S*,*R*)-**4b**	121–123	−295.5°	52.17 (52.90)	7.45 (7.27)	1.63 (1.67)	36.46 (bd, *J*(Rh–P) 154 Hz) 25.87(bs)
(*R*,*S*)-**4b**		+297.2°				
(*S*,*S*)-**5**	147–149	+169.4°	54.12 (54.91)	7.86 (7.93)	1.19 (1.42)	38.02 (d, *J*(Rh–P) 153 Hz) 27.88(s), 25.38(s)
(*R*,*R*)-**5**		−170.8°				

[a] (*c* 1, C_6H_6) for ligands (*c* 0.5, $CHCl_3$) for complexes. [b] C_6D_6 is solvent for ligands; $CDCl_3$ for complexes of **3** and **4**; CD_2Cl_2 for complex of **5**.

TABLE 4

^{1}H NMR DATA FOR LIGANDS (P–N) AND COMPLEXES [(P–N)RhNBD]ClO$_4$ [a]

(P–N) [a]	P(CMe$_3$)$_2$	Others	Complex conformer	CHMe	CMe	NMe$_2$	P(CMe$_3$)$_2$
3b	1.42(d,9,*J*(PH) 12 Hz)	1.38(d, CMe, *J*(HH) 8 Hz)	**A**	3.20(bq)	1.63(d)	3.40(s)	1.76(d, *J*(PH) 12 Hz)
	0.86(d,9,*J*(PH) 12 Hz)	3.57(dq, C*H*Me, *J*(PH) 4 Hz)		(*J*(HH) 8 Hz)	(*J*(HH) 8 Hz)	2.28(s)	1.00(d, *J*(PH) 12 Hz)
		2.11(s, NMe$_2$)					
		4.07(s,(C$_5$H$_5$)Fe)	**B**	4.60	1.53(d)	2.24(s)	1.52(d, *J*(PH) 12 Hz)
		4.16–4.46(m,C$_5$H$_3$)Fe)			(*J*(HH) 8 Hz)	1.78(s)	1.35(d, *J*(PH) 16 Hz)
4b	1.6(d,9,*J*(PH) 12 Hz)	1.35(d,CMe, *J*(HH) 8 Hz)	**A**	3.22(bq)	1.67(d)	3.42(s)	1.00(d, *J*(PH) 16 Hz)
	1.3(d,9,*J*(PH) 12 Hz)	4.00(dq, C*H*Me, *J*(HH) 8, *J*(PH) 4 Hz)		(*J*(HH) 7 Hz)	(*J*(HH) 7 Hz)	2.32(s)	1.09(d, *J*(PH) 12 Hz)
	1.2(d,9,*J*(PH) 12 Hz)	2.20(s,NMe$_2$)					1.24(d, *J*(PH) 12 Hz)
	1.1(d,9,*J*(PH) 12 Hz)	4.1–4.5(m,(C$_5$H$_3$)Fe(C$_5$H$_4$))					1.80(d, *J*(PH) 16 Hz)
			B	4.61	1.55	2.26(s)	1.07(d, *J*(PH) 12 Hz)
						1.80(s)	1.22(d, *J*(PH) 12 Hz)
							1.37(d, *J*(PH) 12 Hz)
							1.58(d, *J*(PH) 12 Hz)
5	1.7(d,9,*J*(PH) 12 Hz)	1.80(d,CMe, *J*(HH) 8 Hz)	**C**	2.97(q)	2.75(d)	1.90(s)	1.59(d, *J*(PH) 16 Hz)
	1.5(d,9,*J*(PH) 10 Hz)	3.80(dq,C*H*Me, *J*(HH) 8, *J*(PH) 4 Hz)		(*J*(HH) 8 Hz)	(*J*(HH) 8 Hz)	2.42(s)	1.41(d, *J*(PH) 12 Hz)
	1.2(d,9,*J*(PH) 12 Hz)	2.40(s,NMe$_2$)					1.40(d, *J*(PH) 12 Hz)
	1.1(d,9,*J*(PH) 12 Hz)	4.4–4.8(m,(C$_5$H$_3$)$_2$Fe)					1.09(d, *J*(PH) 16 Hz)
							0.91(d, *J*(PH) 12 Hz)

[a] Solvents: C$_6$D$_6$ for ligands; CD$_2$Cl$_2$ complexes.

(*S*,*R*)-**4b**, and (*R*,*R*)-**5**, so the mono- and bis-phosphines have the expected configuration (Scheme 1). The CD curves for the two enantiomers of **5** are shown in Fig. 3.

The cationic rhodium(I) complexes [(P–N)RhNBD]ClO$_4$ are easily prepared from the ligands **3b**, **4b**, and **5** as confirmed by the analytical data and spectrscopic properties. The ^{31}P NMR spectra are particularly useful in this regard as they all show only one phosphorus resonance moves by about 20 ppm and becomes a doublet through rhodium coupling. The remaining singlets move only a little on coordination. Thus all three ligands are bound to rhodium by the NMe$_2$ moiety and one P(CMe$_3$)$_2$ group; the data indicate that it is the N and the P on the same ring which bind. Kumada and coworkers believe that rhodium(I) complexes of **4a** are P–P bound [19] and have reported unpublished work in support of this structure for the PdCl$_2$ derivative of **4a** [20]. It seems that the nature of the groups attached to phosphorus exerts a subtle influence on the choice of binding mode [18].

A striking feature of the ^{31}P NMR spectra of the [(P–N)RhNBD]ClO$_4$ complexes is their line shape. The spectra are sharp when (P–N) is **5** but broad when (P–N) is **3b** or **4b**. This indicates the existence of some fluxional process in solution. The ^{1}H NMR spectra (Table 4 and Fig. 4) provide more information.

Figure 4 shows the spectrum of [(P–N)RhNBD]ClO$_4$, ((P–N) = **3b**). The broadness of the spectrum at 35 °C was commented on earlier [2]. The lines sharpen

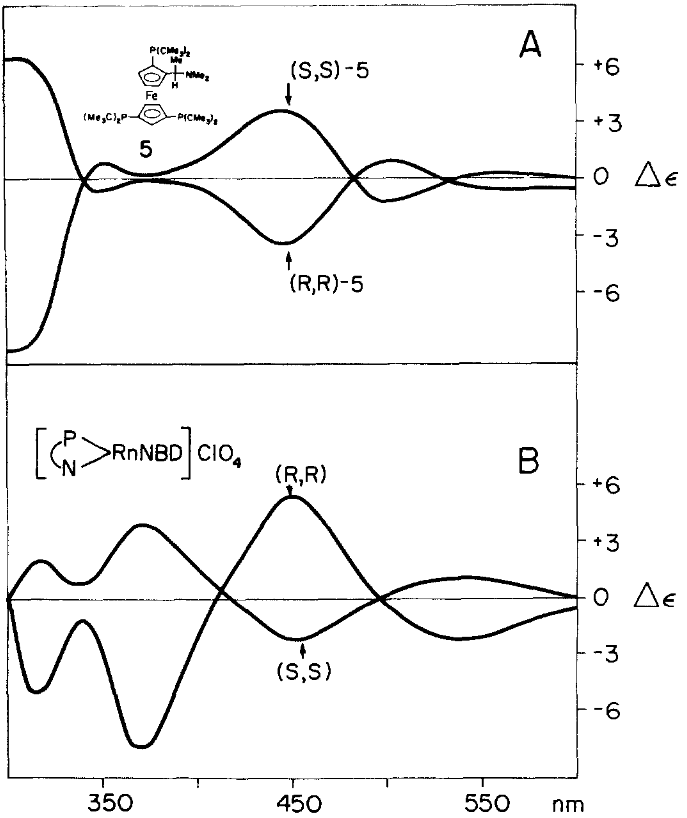


Fig. 3. The CD spectra of the enantiomers of **5**, A, and their rhodium(I) complexes, [(P–N)RhNBD]ClO$_4$, B.

considerably on cooling to 0 °C and the spectrum does not change appreciably on further cooling (− 60 °C). The spectrum can be assigned to two conformers **A** and **B** (Fig. 5). Thus two resonances are seen for the unsubstituted Cp ring designated arbitrarily F_A and F_B. The relationship between C_A (or C_B) ($\overset{*}{C}H$MeNMe$_2$) and M_A (or M_B) ($\overset{*}{C}$H*Me*NMe$_2$) was established by spin decoupling. Assignments to particular conformations were done on the basis of the known structure (P–N) = **3a** [3], and use of models. Thus C_B (the proton on $\overset{*}{C}$) is much further downfield than usually found because in conformer **B** it is almost coplanar with a Cp ring and subjected to a ring current. Similarly $N_A(1)$ is assigned to the Me group of the NMe$_2$ moiety which is downfield because it also is coplanar with a Cp ring.

The assignment of the NMe$_2$ groups to particular conformations was made by

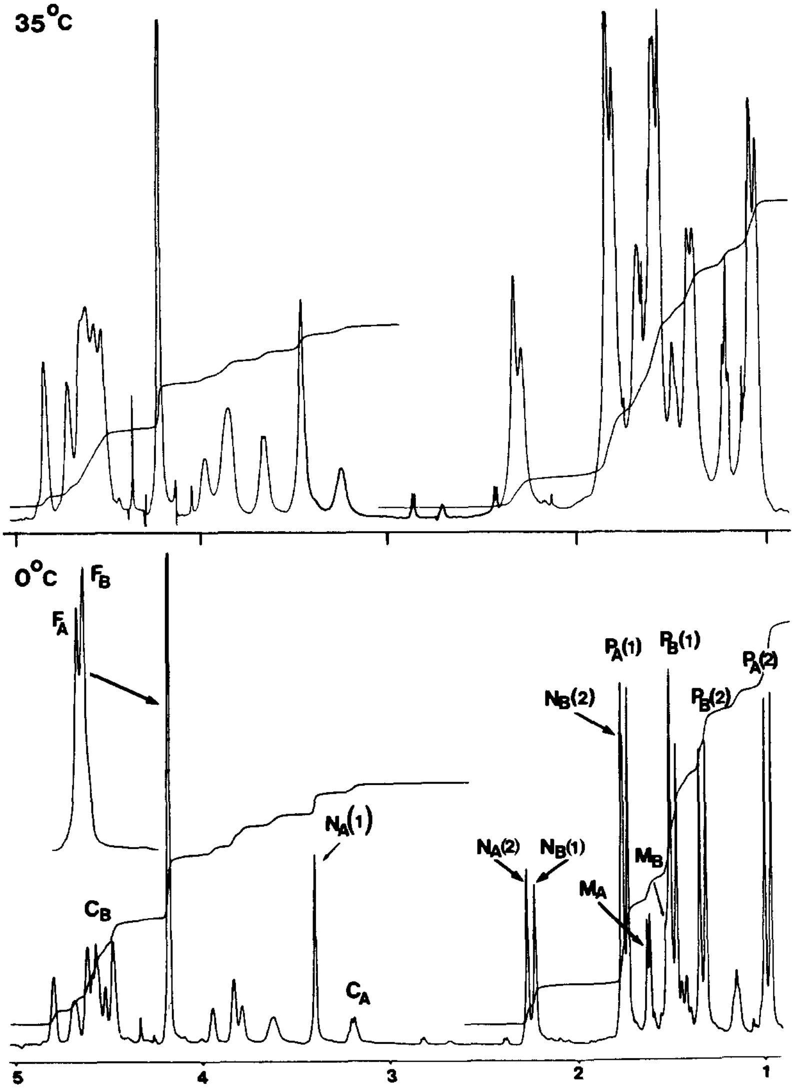
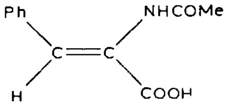
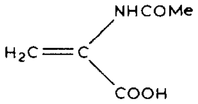
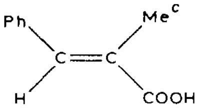
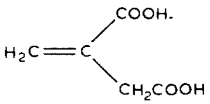


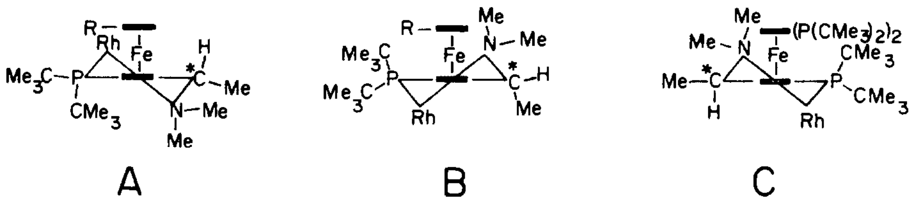
Fig. 4. ^{1}H NMR spectra of [(P–N)RhNBD]ClO$_4$, (P–N) (**5**).

TABLE 5

ASYMMETRIC HYDROGENATION OF SOME OLEFINIC ACIDS WITH $[(P\text{–}N)RhNBD]ClO_4$ [a,b]

Substrate	(P–N)	Time (h)		%e.e.		Configuration
		MeOH	EtOH	MeOH	EtOH	
	(*S*,*R*)-**3a**		24		76	*S*
	(*S*,*R*)-**3b**		16		84	*R*
	(*S*,*R*)-**4b**	3.1	4.3	2	4	*R*
	(*S*,*S*)-**5c**	4.2	4.8	86	91	*S*
	(*S*,*R*)-**3a**		18		49	*S*
	(*S*,*R*)-**3b**		12		24	*R*
	(*S*,*R*)-**4b**	2.5	3.2	14	31	*R*
	(*S*,*S*)-**5**	3.2	3.6	82	95	*S*
	(*S*,*R*)-**4b**	2.3	2.7	51	51	*S*
	(*S*,*S*)-**5**	3.0	3.5	59	61	*R*
	(*S*,*R*)-**3a**		72 [d]		33	*R*
	(*S*,*R*)-**3b**		16		43	*S*
	(*S*,*R*)-**4b**	–	2.3	–	28	*S*
	(*S*,*S*)-**5**	4.5	4.7	19	38	*R*

[a] All reaction involving **4b** and **5** are stoichiometric. [substrate] = 4.0×10^{-2} *M* in 10 ml of solvent; [catalyst precursor] = 4.0×10^{-4} *M*; $P(H_2)$ 1 atm; *T* 30 °C; Time = approximate total reaction time. The data for **3a** and **3b** are taken from ref. 2; here [catalyst] = 5×10^{-4} *M* and [substrate] = 5×10^{-2} *M*. [b] Optical yields are based on the rotation of the isolated products. [c] This gives the (*S*)-isomer (28% e.e.) in benzene (reaction time > 10 h). [d] The chemical yield after 72 h was 21%.



(P–N) = (S,R)-3b ; R = H ; A : B = 1 : 1

(P–N) = (S,R)-4b; R = $P(CMe_3)_2$; A : B = 2 : 1

(P–N) = (S,S)-5 ; C is the only conformer

Fig. 5. The most populated conformers present in solutions of $[(P\text{–}N)RhNBD]ClO_4$ (P–N) (**3b**, **4b** or **5**).

comparison following investigation of the temperature dependent spectra of the complex of the ligand **4b**. In this case two similar conformers are also seen but the relative amounts are different (**A**/**B** 1/2) at 35 °C allowing assignment to **A** or **B**. When the ligand is **5** the spectrum is sharp at 35 °C; cooling indicates that only one conformer, **C**, is present (Table 4, Fig. 4). The downfield shifted Me group is coplanar with the Cp ring.

The CD spectra of the rhodium(I) complexes are almost the reverse of those of the chiral ligands. This is particularly apparent in Fig. 3 with the band at 450 nm. Table 3 gives some hint of this situation as the specific rotation of the ligand and complexes are of opposite sign.

Asymmetric hydrogenation studies

The data obtained in the present investigation are seen in Table 5. The most obvious result is that the derivative of **5** is an exceptionally efficient catalyst for the hydrogenation of the two amino acid precursors. The optical yields are as good as those obtained from more conventional catalysts some of which are as follows for the acylaminocinnamic acid derivative (ligand, optical yield (configuration)) [21]; (*R*,*R*)-DIPAMP, 94%(*S*); (*S*,*S*)-chiraphos, 89(*R*); (*S*,*S*)-skewphos, 93(*R*); (*S*,*R*)-BPPFA 93(*S*) *. It is clear that in spite of recent statements to the contrary [22] PAr_2 donor groups on the ligand are not necessary for producing asymmetric bias let alone the requirement that they be arranged in a chiral array of alternating edges and faces [22].

There are a limited number of examples of the use of metal derivatives of chiral aliphatic phosphines as catalysts for carbonyl group hydrogenation [23] and ketone hydrosilylation [24] but this probably reflects synthetic difficulties rather than any fundamental property.

The results of Table 5 suggest that it is the planar chirality of the ligands which dictates the configuration of the hydrogenation product for a given series i.e. PPh_2 or $P(CMe_3)_2$ (a reversal occurs with **3a** and **3b** as ligands [2] and may occur with **4a** and **4b** (Table 5, and the result for BPPFA (**4a**), given above [6,21]; although **4a**, as also mentioned above, may not be P–N bound in this case). The complex of the trisphosphine **5** exists predominantly as conformer **C**, Fig. 5. The conventional configuration of this is δ for the (*S*,*S*)-ligand [25]. This conformation is also favored by rhodium complexes of (*S*,*S*)-chiraphos and (*S*,*S*)-skewphos [26]; however, the hydrogenation products are enantiomeric with those of (*S*,*S*)-**5** so arguments to explain the configuration of hydrogenation products based on ring conformations should not be extended to these ferrocenylphosphine systems [22,26].

The optical yields listed in Table 5 are very ligand dependent, the most dramatic differences occurring between the derivatives of **4b** and **5**. The complex of (*S*,*S*)-**5** in solution exists in one main conformation δ. Those of **3b** and **4b** have two well populated conformations **A** and **B** (Fig. 5) which have δ and λ conformations respectively for the (*R*,*S*)-ligands. If these conformations function in opposite directions in inducing enantioface discrimination then variable optical yields could

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* Ligand abbreviations are as follows: DIPAMP, $[(1,2\text{-}C_6H_4OMe)PhPCH_2]$; chiraphos, $[Ph_2PCHMe]_2$; skewphos, $(Ph_2P\ CHMe)_2CH_2$; BPPFA (**4a**).

be expected. Such phenomena may account for the reversal of product chirality encountered with the complex of **5** when the hydrogenation is carried out in benzene solution (Table 5, footnote *c*).

The reduction of itaconic acid shown in Table 5 occurs in moderate optical yield and in this case there is not much difference between the complexes of the (P–N) ligands. The same is true for the reduction of α-methylcinnamic acid although in this case the 61% optical yield is as good as any obtained to date [21]. The rate is also significant here as Knowles [22] has pointed out that asymmetric reductions of this substrate are usually very slow.

The mechanism of asymmetric hydrogenation outlined by Bosnich and coworkers [26] based on the results of the groups of Halpern [27] and Brown [28] is implicit in much of the preceding discussion. We have recently established that hydrides are easily formed when hydrogen is passed through solutions of [(P–N)RhNBD]ClO$_4$ [29] (some bis(tertiary phosphine) derivatives [(P–P)RhNBD]ClO$_4$ behave similarly [30]). These hydrides are catalysts for olefin hydrogenation so perhaps some of the peculiarities of the ferrocenylphosphine based systems may be due to their functioning by another, possibly hydride, mechanism. These aspects are under investigation.

Acknowledgments

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