Rhodium and Ruthenium Complexes of 1,1′-Bis(phosphetano)ferrocenes: Structural Characterisation and Catalytic Behaviour

Angela Marinetti,*[a] Francis Labrue,[a] Bénédicte Pons,[a] Sébastien Jus,[a] Louis Ricard,[b] and Jean-Pierre Genêt[a]

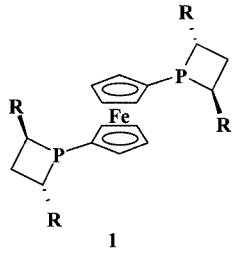
Keywords: Asymmetric catalysis / Hydrogenations / P ligands / Phosphetane / Rhodium / Ruthenium

The first structural characterisation of ruthenium and rhodium complexes of the 1,1′-bis(phosphetano)ferrocenes **1** (FerroTANEs) – namely [{(*S*,*S*)-*i*Pr-**1**}$RuCl_2Py_2$] and [{(*S*,*S*)-*i*Pr-**1**}Rh(COD)OTf] – is reported. X-ray data show that the ruthenium complex and the rhodium chelate complex both adopt δ conformations, as a result of the (*S*,*S*) configuration of the phosphetane moiety. The ruthenium complexes promote the catalytic hydrogenation of β-keto esters with moderate to high enantioselectivities. The behaviour of the rhodium complexes of **1** is compared with that of other phosphetane-based catalysts in the hydrogenation of methyl *N*-acetamidocinnamate.

Introduction

The 1,1′-bis(phosphetano)ferrocenes **1** (FerroTANEs) rank among those ligands that induce excellent enantioselectivities in rhodium-promoted hydrogenations.[1] In particular, their practical utility has been demonstrated in the synthesis of amido succinates by asymmetric hydrogenation of itaconate derivatives.[2] In these reactions, ligands **1** perform better, in terms of efficiency and enantioselectivity, than other well known diphosphanes such as DuPHOS, DIPAMP or PHANEPHOS. Recently, their high efficiency in the catalytic hydrogenation of (*E*)-β-amino acid derivatives has also been established.[3] It thus seems that the combination of a conformationally constrained phosphetane ring with the relatively flexible ferrocene backbone represents a favourable structural feature for high catalytic efficiency. For comparison, the structurally analogous 1,1′-bis(phospholanyl)ferrocenes give only moderate to low enantioselectivities in hydrogenation reactions.[4]

Besides their good catalytic properties, the potential utility of diphosphanes **1** is also founded on their easy availability: diphosphanes **1** are easily accessible from fairly inexpensive chiral 1,3-diols and their structures and catalytic properties are easily and finely tuned by variation of the R groups at the α-positions of the phosphetane rings.



1

Following our initial report on the synthesis and preliminary catalytic screening of these ligands, we wish to disclose here the preparation and first structural characterisation of ruthenium and rhodium complexes of **1**, which are efficient catalyst precursors for hydrogenation reactions. Additional data on their catalytic properties is also reported.

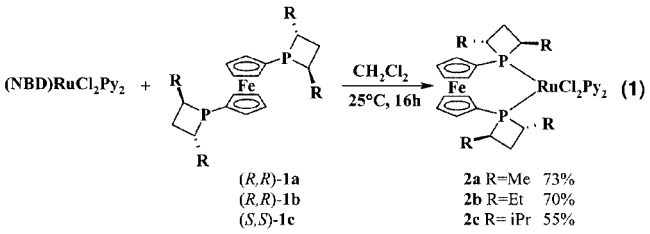
Results and Discussion

Crystal Structures of the [(*S*,*S*-1c)$RuCl_2(Py)_2$] and [(COD)Rh(*S*,*S*-1c)OTf] Complexes

With regard to the excellent catalytic properties of the 1,1′-bis(phosphetano)ferrocenes **1**, it is highly interesting to investigate the coordinating behaviour of these new ligands towards catalytically active transition metals, as well as the structural features of their complexes. With this aim, we prepared the [{(*S*,*S*)-*i*Pr-**1**}$RuCl_2(Py)_2$] complex **2**, which is a potential precursor for hydrogenation catalysts. The synthesis of **2** was performed according to the Bergens procedure:[5] the reaction between **1** and the [(NBD)$RuCl_2Py_2$] complex (NBD = norbornadiene, Py = pyridine) at room temperature. Facile and quantitative displacement of the

[a] Laboratoire de Synthèse Sélective Organique et Produits Naturels – ENSCP,
11, rue Pierre et Marie Curie, 75231 Paris Cedex 05, France
Fax: (internat.) + 33-1/4407 1062
E-mail: marinet@ext.jussieu.fr
[b] Laboratoire Hétéroéléments et Coordination – Ecole Polytechnique,
91128 Palaiseau Cedex, France

unsaturated ligand by the chelating diphosphane is observed, as shown in Equation (1).



The ruthenium complexes **2** are obtained in moderate to high yields after crystallisation from dichloromethane/pentane mixtures, as air-stable, orange, crystalline solids. NMR spectroscopy shows that complexes **2** have C_2-symmetrical structures, with equivalent phosphetane and also pyridine moieties. The ^{31}P NMR resonance of complexes **2** is shifted downfield with $\Delta\delta$ of 60−70 ppm relative to **1**, the less hindered complex **1a** undergoing the larger shift upon coordination.

The first structural characterisation of any 1,1′-bis(phosphetano)ferrocene−transition metal derivative has been performed on complex **2c**. An ORTEP drawing is shown in Figure 1, and selected bond lengths and angles are reported in Table 1.

Complex **2c** crystallises in the orthorhombic system, with one dichloromethane molecule per molecular unit. The ruthenium atom is approximately octahedral. The bis-equatorially coordinated diphosphane gives a P−Ru−P bite angle of 98.57(3)°, in good agreement with the expected value, as large deflections from the ideal 90° (metal natural bite angle) up to about 100° are usually observed in square-planar and octahedral complexes of dppf[6] and other 1,1′-bis(phosphanyl)ferrocenes.[7] The conformation of the Cp rings is staggered, with a torsion angle of 45.7°. The rotation of the cyclopentadienyl rings against each other, together with their tilt, produces a fairly large P−P distance of 3.51 Å (as compared with the Cp−Cp′ distances of 3.28 Å).

Table 1. Selected interatomic distances [Å] and angles [deg] for complex **2c**

Ru(1)−P(1)	2.321(1)	Ru(1)−Cl(2)	2.437(1)
Ru(1)−P(2)	2.319(1)	P(1)−C(1)	1.892(3)
Ru(1)−N(1)	2.231(3)	P(1)−C(3)	1.887(3)
Ru(1)−N(2)	2.170(3)	P(2)−C(11)	1.908(3)
Ru(1)−Cl(1)	2.425(1)	P(2)−C(9)	1.884(3)
P(1)−Ru(1)−P(2)	98.57(3)	C(1)−P(1)−C(3)	76.3(1)
N(1)−Ru(1)−N(2)	81.7(1)	C(4)−P(1)−Ru(1)	119.9(1)
P(1)−Ru(1)−N(1)	90.20(7)	C(11)−P(2)−C(12)	77.3(2)

The structural parameters of the phosphetane rings show standard values, with small intracyclic C−P−C angles of 76.3(1) and 77.3(2)°, respectively, and ring bending angles of 25.5 and 17.6°, respectively.

A significant structural feature of the complex is the δ conformation[8] adopted by the ferrocene backbone, which enforces a dissymmetric coordination of the phosphetane rings (see Figure 2): the C(3) and C(9) ring atoms, and the corresponding isopropyl substituents, are shifted away from the ruthenium coordination plane, in pseudoaxial positions, while the C(1) and C(11) atoms occupy pseudoequatorial positions. The corresponding dihedral angles between the P(1)−Ru−P(2) plane and the P−C axis are −93°

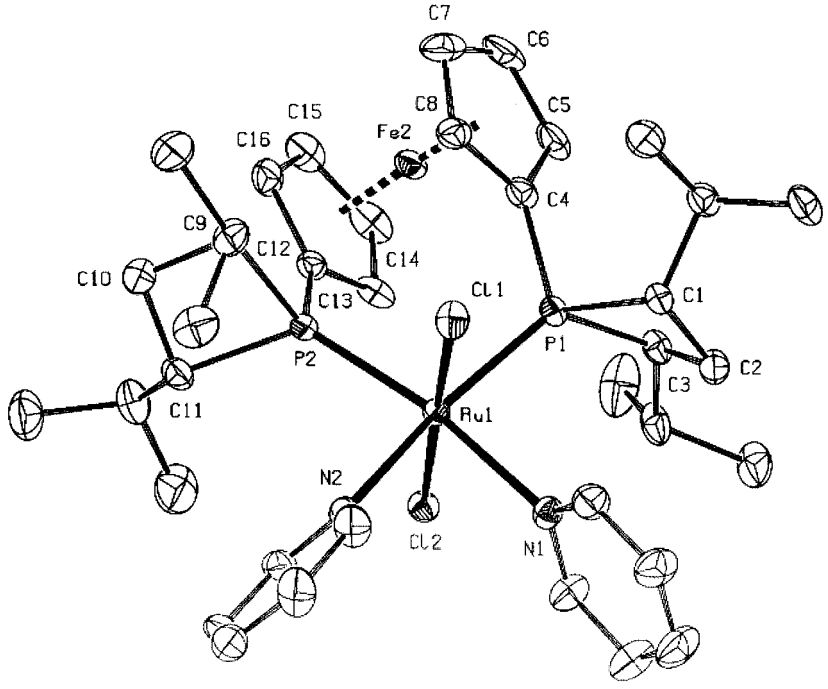


Figure 1. ORTEP drawing for the ruthenium complex **2c**

[P(1)−C(3)], 163° [P(1)−C(1)], −128° [P(2)−C(9)] and 141° [P(2)−C(11)]. The δ conformation of the ferrocene backbone therefore tends to minimise the steric hindrance between the isopropyl groups, which are oriented toward the metal, and the other ligands in the equatorial coordination plane of ruthenium. In a sense, this also balances the dissymmetry of the ruthenium environment created by the chiral phosphetane units and could decrease the asymmetric discrimination from these ligands somewhat.

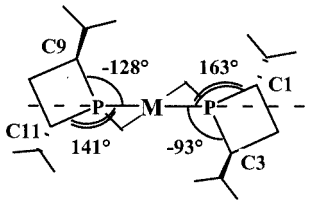


Figure 2. Coordination mode of the bis(phosphetano)ferrocene moiety in the ruthenium complex **2c**

A similar coordination mode is observed in the rhodium complex **3c**, containing the same ligand **1c**. An ORTEP drawing and selected bond angles and distances for complex **3c** are shown in Figure 3 and Table 2, respectively.

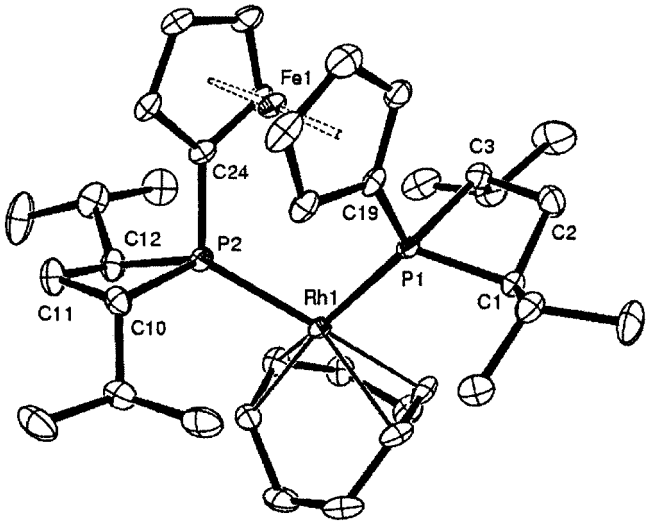


Figure 3. ORTEP drawing of the [(COD)Rh(**1c**)OTf] complex **3c**

Table 2. Selected interatomic distances [A°] and angles [deg] for complex **3c**

Rh(1)−P(1)	2.324(1)	C(1)−C(2)	1.570(5)
Rh(1)−P(2)	2.317(1)	C(2)−C(3)	1.554(6)
P(1)−C(1)	1.877(4)	P(2)−C(10)	1.885(3)
P(1)−C(3)	1.884(4)	P(2)−C(12)	1.869(4)
P(1)−C(19)	1.810(3)	P(2)−C(24)	1.813(3)
P(1)−Rh(1)−P(2)	96.90(3)	C(1)−P(1)−C(3)	78.1(2)
C(19)−P(1)−Rh(1)	121.5(1)	C(10)−P(2)−C(12)	77.9(2)

Phosphetane **1c** thus generally seems to favour δ conformations in its transition metal complexes, as a result of its (*S*,*S*) stereochemistry.

Ruthenium-Promoted Hydrogenations of β-Keto Esters

As shown by Bergens, many [(diphosphane)$RuCl_2Py_2$] complexes afford efficient hydrogenation catalysts after treatment with acids. This is also the case for complexes **2**: when activated by addition of four equivalents of HBr, these complexes catalyse the asymmetric hydrogenation of carbonyl derivatives. Methyl acetoacetate and ethyl isobutyrylacetate were selected as model substrates for the hydrogenation reactions (Table 3).

Under the conditions given (see Table 3), ligands **1a**−**c** display moderate to high enantioselectivities as a function of the phosphetane α-substituents: the enantiomeric excesses of the final β-hydroxy esters increase significantly with increasing steric hindrance of the ligand. Thus, for instance, *ee*s of 44%, 56%, and 80% were obtained in the hydrogenation of methyl acetoacetate with use of ligands **1a**, **1b**, and **1c**, respectively. The observed trend contrasts with the behaviour of the same ligands in rhodium-promoted hydrogenations of olefinic substrates, where the best enantioselectivities are attained with the 2,4-diethyl-substituted ligand.[2] This once again confirms the need for highly specific tuning of the ligand substituents for any given reaction.

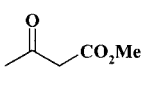
Two other ruthenium catalyst precursors were evaluated under the above hydrogenation reactions: catalysts were formed in situ from **1a**−**c** and $[(C_6H_6)RuCl_2]_2$ or [(COD)-Ru(2-methylallyle)$_2$],[9] by known procedures. Selected results are given in Table 3. Both catalytic systems give activities and enantioselectivities either comparable to or somewhat lower than those obtained with complexes **2**. Thus, in our hands, complexes **2** were the most suitable catalyst precursors, being well defined, bench-stable and easy to handle.

The few catalytic tests above show that the 1,1′-bis(phosphetano)ferrocenes **1** afford moderate catalytic activities and quite high, albeit not magnificent, enantioselectivities in ruthenium-promoted hydrogenations of carbonyl derivatives. At first sight it seems that, in these reactions, ligands **1** will be not very competitive with other chiral ligands,[10] and especially with atropisomeric diphosphanes.[11] Of course, this cannot be regarded as a final settlement, as very few substrates, catalytic systems, and conditions have been evaluated. Fine tuning of the phosphetane substituents and/or of the reaction conditions could allow better achievements.

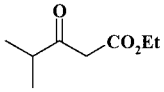
Rhodium-promoted Hydrogenations of Functionalised Olefins

The catalytic efficiency of 1,1′-bis(phosphetano)ferrocenes **1** in rhodium(I)-promoted hydrogenations of functionalised olefins has already been established.[1−3] The main purpose of this study was to gain insight into their behaviour in these reactions, in comparison with that of other phosphetane-based ligands, namely CnrPHOS[12] and BPE-4.[13]

Table 3. Asymmetric hydrogenation of β-keto esters



4



5

Substrate	Ligand	Ru precatalyst	Conditions[a]	Conv. (%)	*ee* (config.)
4	**1a**	(**1a**)$RuCl_2Py_2$ + HBr	(a)	100	44 (*R*)
	1a	$(COD)Ru(C_4H_7)_2$ + HBr	(b)	100	11 (*R*)
	1b	(**1b**)$RuCl_2Py_2$ + HBr	(a)	100	56 (*R*)
	1c	(**1c**)$RuCl_2Py_2$ + HBr	(a)	100	**80 (*R*)**
5	**1a**	(**1a**)$RuCl_2Py_2$ + HBr	(a)	31	53 (*S*)
	1a	$(COD)Ru(C_4H_7)_2$ + HBr	(b)	36	58 (*S*)
	1b	(**1b**)$RuCl_2Py_2$ + HBr	(b)	50	80 (*S*)
	1c	(**1c**)$RuCl_2Py_2$ + HBr	(a)	40	**84 (*S*)**
	1c	$[(C_6H_6)RuCl_2]_2$	(a)	40	64 (*S*)
	1c	$[(C_6H_6)RuCl_2]_2$	(c)	100	63 (*S*)

[a] Reaction conditions: 1 mmol substrate, S/C = 100, MeOH (1 mL) as solvent, reaction time 24 h−48 h; (a) 50 °C; 10 bar H_2, (b) 50 °C; 80 bar H_2, (c) 80 °C, 10 bar.

More precisely, we examine here the enantioselectivity of the catalytic hydrogenation of dehydro amino acid derivatives, as a function of several experimental parameters. An analogous study on the CnrPHOS and BPE ligands highlighted, among other things, an unusually strong effect of the hydrogen pressure on the enantioselectivity, with higher *ee*s being obtained at higher pressures.[14] The preliminary data on this phenomenon were confirmed by the additional experiments shown in Table 4 and Figure 4. Methyl α-acetamidocinnamate **6** was hydrogenated, at various hydrogen pressures, in the presence of a rhodium catalyst generated in situ from $[Rh(COD)_2OTf]$ and (*S*,*S*)-CyBPE-4. Mechanical stirring was applied to ensure efficient adsorption of H_2 into the solution. For comparison, the *ee*s obtained with magnetic stirring are reported in entry 1 (from ref.[14]): mechanical stirring improves the enantioselectivity of reactions performed under otherwise identical conditions. This is probably related to more efficient and homogeneous dihydrogen exchange between gas and liquid phases.

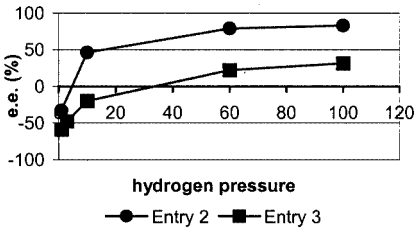
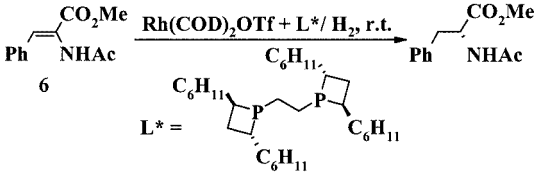


Figure 4. Plotting of data from Entries 2 and 3 in Table 4

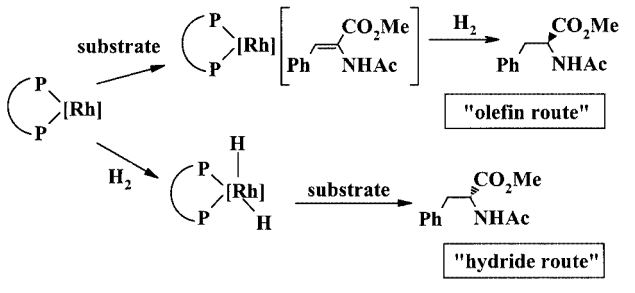
Table 4. Enantiomeric excesses of the *N*-acetylphenylalanine methyl ester obtained from **6** by Rh/(*S*,*S*)-CyBPE-4-promoted hydrogenations



		P(H_2) - bar				
Entry	Solvent	1	3	10	60	100
1[a]	C_6H_6/CH_2Cl_2 : 4/1			15 (*R*)		70 (*R*)
2	C_6H_6/CH_2Cl_2 : 4/1	33 (*S*)	-	46 (*R*)	79 (*R*)	**83** (*R*)
3	CH_2Cl_2	**59** (*S*)	48 (*S*)	20 (*S*)	22 (*R*)	31 (*R*)

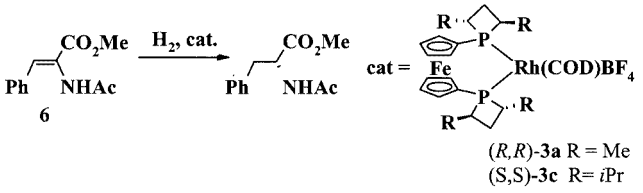
[a] From ref.[14] 1% catalyst, substrate concentration: 0.1 M, room temperature.

Two series of experiments were performed, in CH_2Cl_2 and in a C_6H_6/CH_2Cl_2 mixture (4:1). The expected significant effect of hydrogen pressure on stereoselectivity was observed in each case: increased hydrogen pressure clearly favours formation of the *R* enantiomer, while the *S* enantiomer predominates at low pressures. The enantioselectivity levels depend on the solvent used, higher *ee*s being attained in the benzene/dichloromethane mixtures. Mechanistic implications of analogous results have already been discussed in our preliminary communication. Most probably, the reversal of stereoselectivity should be related to some form of "tilting" over to a new reaction pathway which operates at



higher pressures. According to the most recent studies on rhodium-promoted enamide hydrogenation with electron-rich phosphanes,[15] competition between the "olefin" and the "hydride" mechanisms, operating at high pressure, seems to be a reasonable hypothesis.

After the above studies, we wondered whether the ferrocenyl-substituted phosphetanes **1** would or would not display analogous behaviour in rhodium-promoted hydrogenations. We therefore examined the pressure effect in the hydrogenation of the dehydroamino esters **6** with the preformed complexes **3** as the catalyst precursors.



From the data in Table 4 it appears that the pressure/enantioselectivity relationship for phosphetanes **1a** and **1c** does not follow the same trend as for Cy-BPE-4 and CnrPHOS: a slight decrease in the enantioselectivity is observed at higher pressure, both in dichloromethane/benzene mixtures and in methanol as solvents (see entries 1, 2, 5, and 6). This suggests that the pressure effect observed with Cy-BPE-4 and CnrPHOS cannot be assigned specifically to their phosphetane-type structures; their catalytic behaviour should be influenced by their whole structures. In particular, their electronic properties should be crucial, as it has been demonstrated that the stereochemical issue of the hydrogenation of dehydroamino acid derivatives is mainly governed by the electron-donating power of the diphosphane ligands.[14]

FerroTANEs **1** simply behave like other electron-rich diphosphanes such as DuPHOS[16] or BisP,[17] the (*S*,*S*)-configured ligand **1c** giving the expected (*R*)-configured product in good enantiomeric excesses. The enantiomeric excesses are then slightly modulated by hydrogen pressure, as well as by any other experimental conditions, in the usual manner.

Thus far, the best conditions for the hydrogenation of **6** are the following: phosphetane **1a** as the ligand, 1 bar of H_2 pressure, MeOH as the solvent, and a reaction temperature of about 50 °C. An enantiomeric excess of 96% is obtained.

The results in Table 5 also suggest that hydrogenation reactions with ligands **1a** and **1c** require slightly different optimal conditions. Fine tuning of the reaction conditions is thus required for each ligand-substrate couple in order to attain the highest selectivities, even within a single series of ligands.

When a different substrate is considered, optimisation is once again necessary, as variation of the experimental parameters has unpredictable effects on enantiomeric excesses. In the hydrogenation of methyl acetamidoacrylate with complex **3c**, for instance, we have observed that an increased H_2 pressure improves the enantioselectivity from 87%, under 1 bar pressure, to 94% under 5 bar (at room temperature, in MeOH; *R* enantiomer).

Table 5. Enantiomeric excesses of the catalytic hydrogenations promoted by complexes **3a** and **3c**; all experiments give the *R*-configured β-amino ester

				P(H_2)				
Entry	Solvent	Catalyst	T °C	1	5	10	30	50
1	C_6H_6/CH_2Cl_2 : 4/1	**3c**	23	87	86	85	78	75
2	C_6H_6/CH_2Cl_2 : 4/1		50	75	74			
3	MeOH		23		83			
4	C_6H_6/CH_2Cl_2 : 4/1	**3a**	23		83			
5	MeOH		23	94	90		86	
6	MeOH		50	**96**	91			

The electron-rich character of P-ferrocenyl-substituted phosphetanes was ascertained by IR spectroscopy of the [Cl(CO)Rh{(*R*,*R*)-1-ferrocenyl-2,4-dimethylphosphetane}] complex **7a**.

The ν(CO) value for the ferrocenyl-substituted phosphetane complex **7a** appears at lower frequency than in the analogous *P*-phenylphosphetane complex **7c**, within the range expected for electron-rich phosphanes. For comparison, the ν(CO) values for analogous rhodium complexes of cyclic and acyclic phosphanes are reported in Table 6. The data in Table 6 also suggest that phosphetanes are poorer donating ligands than the corresponding phospholanes, as an effect of ring size.

Table 6. ν(CO) values for the [Cl(CO)RhL_2] complexes **7**

Complex		**7a**		**7b**	**7c**
L	PEt_3		$PhPEt_2$		
ν(CO) cm^{-1} (CH_2Cl_2)	1955[18]	1956	1962[18]	1963	1969

In summary, the hydrogenation reactions of dehydro amino acid derivatives promoted by rhodium complexes of the 1,1′-bis(phosphetano)ferrocenes **1** do not display the unusual pressure/enantioselectivity relationship shown by other C_2-symmetric bis(phosphetane) ligands. Ligands **1** behave like electron-rich diphosphanes and afford significantly high enantioselectivities under optimised experimental conditions.

Experimental Section

All reactions were performed under inert atmosphere (Ar) by use of Schlenk techniques. Solvents were purified according to standard

procedures. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM 400 at 400.13 Hz, 100.6 Hz, and 162 Hz, respectively. HPLC was performed on a Waters 600 chromatograph equipped with a variable wavelength detector and Daicel Chiracel OD-H column. Optical rotations were measured on a Perkin−Elmer 241 polarimeter, with a 1 dm cell. IR spectra were recorded on a Bruker IFS 48 instrument.

General Procedure for the Synthesis of *trans*-[RuCl$_2${1,1′-Bis(dialkylphosphetanyl)ferrocene}Py$_2$] (2): A solution of *trans*-[RuCl$_2$(NBD)Py$_2$][5] (100 mg, 0.23 mmol) and ligand **1** (0.23 mmol) in CH_2Cl_2 (13 mL) was stirred overnight at room temperature. The solvent was removed under vacuum and the residue was recrystallized from a dichloromethane/pentane mixture to afford complexes **2** as yellow, crystalline solids.

***trans*-[RuCl$_2${1,1′-Bis[(*R*,*R*)-2,4-dimethyl-1-phosphetanyl]ferrocene}Py$_2$] (2a):** Yield 120 mg, 73%. ^{31}P NMR ($CDCl_3$): δ = 87. ^{1}H NMR ($CDCl_3$): δ = 9.6 (br., 4 H), 7.60 (m, 2 H), 7.3 (br., 4 H), 5.14 (br. s, 2 H, CH_{cp}), 4.50 (m, $J \approx 1$ Hz, 4 H, CH_{cp}), 4.34 (m, $J \approx 1$ Hz, 2 H, CH_{cp}), 2.66 (m, 2 H), 2.40 (m, 4 H), 1.79 (m, 2 H), 1.28 (dd, $^3J_{H,H}$ = 7.7, $^3J_{P\text{-}H}$ = 16.4 Hz, 6 H, CH_3), 0.92 (dd, $^3J_{H,H}$ = 6.3, $^3J_{P\text{-}H}$ = 14.4 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.6 (br., CH_{Py}), 152.1 (br., CH_{Py}), 136.0 (CH_{Py}), 123.6 (br., CH_{Py}), 123.4 (br., CH_{Py}), 77.6 (t, J = 7.8 Hz, CH_{Cp}), 74.0 (t, J = 3.4 Hz, CH_{Cp}),73.0 (m, AXX′, C_{Cp}P), 72.0 (CH_{Cp}), 71.0 (t, J = 1.8 Hz, CH_{Cp}), 40.1 (t, J = 7.6 Hz, CH_2), 32.0 (m, AXX′, PCH), 30.2 (m, AXX′, PCH), 18.8 (CH_3), 17.5 (t, J = 2.3 Hz, CH_3) ppm. $[\alpha]_D = -782$ (c = 0.2, $CHCl_3$). $C_{30}H_{38}Cl_2FeN_2P_2Ru$ (716.028): calcd. C 50.30, H 5.35, N 3.91; found C 50.66, H 5.96, N 3.82.

***trans*-[RuCl$_2${1,1′-Bis[(*R*,*R*)-2,4-diethyl-1-phosphetanyl]ferrocene}Py$_2$] (2b):** Yield 124 mg, 70%. ^{31}P NMR ($CDCl_3$): δ = 82 ppm. ^{1}H NMR ($CDCl_3$): δ = 9.6 (br., 4 H), 7.60 (t, $J_{H,H}$ = 7.4 Hz, 2 H,CH), 7.3−7.0 (br., 4 H, CH), 5.10 (s, 2 H, CH_{cp}), 4.50 (s br, 4 H, CH_{cp}), 4.32 (m, 2 H, CH_{cp}), 2.77 (br., 2 H), 2.40 (br., 2 H), 2.22 (m, 2 H), 2.04−1.95 (m, 4 H), 1.70 (m, 2 H), 0.87 (m, 4 H), 0.79 (t, $^3J_{H,H}$ = 6.9 Hz, 6 H, CH_3), 0.57 (t, $^3J_{H,H}$ = 7.4 Hz, 6 H, CH_3) ppm. ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 152.4 (br., CH_{Py}), 136.0 (CH_{Py}), 123.4 (br., CH_{Py}), 77.5 (t, J = 7.8 Hz, CH_{Cp}), 74.0 (t, J = 3.4 Hz, CH_{Cp}), 73.5 (m, AXX′, C_{Cp}P), 72.0 (CH_{Cp}), 70.8 (CH_{Cp}), 39.2 (m, AXX′, PCH), 37.6 (m, AXX′, PCH), 34.0 (t, J = 7.3 Hz, CH_2), 25.7 (CH_2CH_3), 23.8 (CH_2CH_3), 13.0 (t, J = 7.5 Hz, CH_3), 12.0 (t, $J_{P,C}$ = 5.9 Hz, CH_3) ppm. $[\alpha]_D = -907$ (c = 0.5, $CHCl_3$). $C_{34}H_{46}Cl_2FeN_2P_2Ru$ (772.091): calcd. C 52.86, H 6.00, N 3.63; found C 52.41, H 6.32, N 3.76.

***trans*-[RuCl$_2${1,1′-Bis[(*S*,*S*)-2,4-diisopropyl-1-phosphetanyl]ferrocene}Py$_2$] (2c):** Yield 105 mg (55%). ^{31}P NMR ($CDCl_3$): δ = 71. ^{1}H NMR ($CDCl_3$): δ = 9.68 (br., 2 H, CH_{Py}), 9.61 (br., 2 H, CH_{Py}), 7.57 (t, $J_{H,H}$ = 7.2 Hz, 2 H, CH_{Py}), 7.19 (br., 2 H, CH_{Py}), 7.09 (br., 2 H, CH_{Py}), 5.29 (s, 2 H, CH_{Cp}), 4.51 (s, 2 H, CH_{Cp}), 4.45 (s, 2 H, CH_{Cp}), 4.28 (m, J≈2 Hz, 2 H, CH_{Cp}), 3.10 (m, 2 H), 2.77 (m, 2 H), 2.0 (m, 4 H), 1.75 (m, 2 H), 1.44 (m, 2 H), 1.05 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 0.79 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3), 0.59 (d, $^3J_{H,H}$ = 6.7 Hz, 6 H, CH_3), 0.56 (d, $^3J_{H,H}$ = 6.6 Hz, 6 H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 153.7 (CH_{Py}), 153.0 (CH_{Py}), 135.9 (CH_{Py}), 123.8 (CH_{Py}), 123.1 (CH_{Py}), 77.9 (CH_{Cp}), 73.7 (CH_{Cp}), 73.2 (C_{Cp}P), 72.4 (CH_{Cp}), 70.3 (CH_{Cp}), 46.4 (m, PCH), 44.0 (m, PCH), 29.2 (CH), 27.8 (CH_2), 24.5 (CH_3), 23.5 (CH_3), 19.8 (CH_3), 19.2 (CH_3) ppm. For crystal data see Table 7.

Table 7. Crystal structure determination for compound **2c**

Empirical formula	$C_{39}H_{56}Cl_4FeN_2P_2Ru$
Formula mass	913.52
Crystal habit	tan needles
Crystal dimensions [mm]	0.20 × 0.14 × 0.14
Crystal system	orthorhombic
Space group	*P*212121
a [Å]	9.651(5)
b [Å]	19.366(5)
c [Å]	22.000(5)
α [°]	90.000(5)
β [°]	90.000(5)
γ [°]	90.000(5)
V [Å^3]	4112(3)
Z	4
d [g·cm^{-3}]	1.476
*F*000	1888
μ [cm^{-1}]	1.088
Absorption corrections	0.8118 min
0.8626	max
Diffractometer	KappaCCD
X-ray source	Mo-*K*α
λ [Å]	0.71069
Monochromator	graphite
T [K]	150.0(10)
Scan mode	phi
Maximum *q*	30.02
hkl ranges	−13 13; −27 27; −30 30
Reflections measured	11960
Independent reflections	11960
R_{int}	0.0000
Reflections used	11161
Criterion	> 2σ(*I*)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	450
Reflections / parameter	24
wR	20.0965
*R*1	0.0353
Flack's parameter	0.006(17)
Weighs *a*, *b*1	0.0380; 5.3251
GoF	1.072
difference peak / hole [e Å^{-3}]	0.767(0.090) / −0.944(0.090)

General Procedure for Hydrogenations Carried out with Complexes 2 as Catalyst Precursors: Hydrogenation experiments were carried out at a 1 mmol scale. The ruthenium complex **2** ($1\cdot10^{-2}$ mmol) was weighed into a small glass reactor fitted with a rubber septum and flushed with argon. Degassed MeOH (1 mL) and then a solution of HBr_{aq} in MeOH (0.16 M, 0.25 mL, 4 equivalents) were added with stirring at room temperature. After a few minutes, the substrate was introduced by syringe. The reaction vessel was placed in a stainless steel autoclave under argon. The argon atmosphere was replaced by hydrogen at the given pressure. The reaction was allowed to proceed for 24−48 h at the temperature given in Table 3. Conversion rates were determined by ^{1}H NMR spectroscopy. The enantiomeric excesses of the final alcohols were determined by chiral CG and the absolute configurations were assigned from the GC retention times by comparison with known samples. **Methyl 3-hydroxybutyrate**: Lipodex A, flow 1 mL·min^{-1}, initial temperature 35 °C (30 min), rate 1 °C·min^{-1}, final temperature 70 °C; retention times 45 (*S*) and 48 (*R*) min. **Ethyl 4-methyl-3-hydroxypentanoate**: Lipodex A, flow 1 mL·min^{-1}, initial temperature 50 °C (5 min),

rate 0.5 °C·min^{-1}, final temperature 70 °C; retention times 48.6 (*S*) and 49.2 (*R*) min.

Preparation of other Catalyst Precursors: (a) According to ref.[9] [(cod)Ru(2-methylallyl)$_2$] (3.2 mg, 1·10^{-2} mmol) and FerroTANE **1** (1.1·10^{-2} mmol) were dissolved in acetone (1 mL) under argon. An HBr_{aq} solution (0.16 M in MeOH, 137 μL, 2.2 equivalents) was then added at room temperature, and the mixture was stirred for 30 min. The solvent was evaporated and the crude residue was taken up in degassed MeOH and used as the catalyst for the hydrogenation reactions (see Table 3). (b) The catalyst precursor was prepared at room temperature by mixing the [(benzene)$RuCl_2$]$_2$ complex (2.5 mg) with **1** in a 1:2 ratio, in CH_2Cl_2 at room temperature. After evaporation of the solvent, the crude residue was used as the catalyst precursor.

General Procedure for the Synthesis of the [(COD)Rh(1)OTf] Complexes 3: A dichloromethane solution of diphosphane **1** (0.2 mmol, 1 mL CH_2Cl_2) was added dropwise, at room temperature, to a solution of $(COD)_2RhOTf$ (93 mg, 0.2 mmol) in the same solvent (1 mL). After the mixture had been stirred for about 15 min, the solvent was removed and the residue was recrystallised either from a dichloromethane/ether mixture (for **3c**) or from a dichloromethane/pentane mixture (for **3a**) to afford a yellow-orange solid.

[(COD)Rh{1,1′-Bis[(*R*,*R*)-2,4-dimethyl-1-phosphetanyl]ferrocene}OTf] (3a): Yield 97 mg, 65%. ^{31}P NMR ($CDCl_3$): δ = 65 (d, $J_{P\text{-}Rh}$ = 147 Hz) ppm. ^{1}H NMR ($CDCl_3$): δ = 5.8 (br. m, 2 H, CH_{COD}), 5.15 (br. m, 2 H, CH_{COD}), 4.70 (s, 2 H, CH_{Cp}), 4.66 (s, 2 H, CH_{Cp}), 4.62 (s, 2 H, CH_{Cp}), 4.37 (s, 2 H, CH_{Cp}), 1.65 (dd, $^3J_{H\text{-}P}$ = 19.7, $^3J_{H,H}$ = 7.6 Hz, 6 H, CH_3), 0.99 (dd, $^3J_{H\text{-}P}$ = 16.3, $^3J_{H,H}$ = 7.0 Hz, 6 H, CH_3) ppm.

[(COD)Rh{1,1′-Bis[(*S*,*S*)-2,4-diisopropyl-1-phosphetanyl]ferroceneOTf} (3c): Yield 120 mg, 70%. ^{31}P NMR ($CDCl_3$): δ = 47 (d, $J_{P\text{-}Rh}$ = 146 Hz). ^{1}H NMR ($CDCl_3$): δ = 5.56 (br. m, 2 H, CH_{COD}), 4.90 (br. m, 2 H, CH_{COD}), 4.80 (s, 2 H, CH_{Cp}), 4.60 (s, 4 H, CH_{Cp}), 4.37 (s, 2 H, CH_{Cp}), 2.2−2.8 (18H), 2.05 (q, *J* = 10.1 Hz, 2 H), 1.84 (d, $^3J_{H,H}$ = 6.5 Hz, 6 H, CH_3), 1.15 (d, $^3J_{H,H}$ = 6.1 Hz, 6 H, CH_3), 0.70 (d, $^3J_{H,H}$ = 6.3 Hz, 6 H, CH_3), 0.69 (d, $^3J_{H,H}$ = 5.5 Hz, 6 H, CH_3) ppm. $C_{37}H_{56}F_3FeO_3P_2RhS{\cdot}CH_2Cl_2$ (942.132): calcd. C 48.37, H 6.20; found C 49.80, H 6.56. For crystal data see Table 8.

The triflate anion (near −0.37, 0.10, 0.31) was highly disordered. Attempts to generate disorder (Shelxl FRAG and PART) all resulted in some non-positive thermal displacement parameters. Consequently, it was decided to account for its electron density by use of the Platon SQUEEZE function.

Rhodium-Promoted Hydrogenations of Methyl α-Acetamidocinnamate: The hydrogenation experiments described in Table 4 were performed in a Teflon-coated autoclave, with mechanical stirring. The rhodium catalyst was prepared at room temperature by mixing [$(COD)_2RhOTf$] (11.2 mg, 2.4·10^{-2} mmol) and (*S*,*S*)-Cy-BPE-4 (14.4 mg, 2.8·10^{-2} mmol) in CH_2Cl_2 (2 mL) for about 10 min. A degassed solution of the substrate (525 mg, 2.4 mmol) in 18 mL of solvent (CH_2Cl_2 or CH_2Cl_2/C_6H_6, 1:4 mixture) was then added and the system was pressurised with dihydrogen. The reaction time was about 24 h. The catalyst was removed by filtration through a short alumina column, with a cyclohexane/ethyl acetate mixture (1:1) as the eluent. Enantiomeric excesses were determined either by chiral HPLC or by chiral GC. The absolute configuration was assigned from the retention times by comparison with known samples. HPLC: Chiracel OD-H column, hexane/2-propanol (90:10), retention times: 11.5 min (*R*) and 14.8 min (*S*). GC: Chirasil-L-Val column, flow = 1 mL/min, *T* = 140 °C, retention times: 37 min (*R*), 39 min (*S*).

Table 8. Crystal structure determination for compound **3c**

Molecular formula	$C_{37}H_{56}F_3FeO_3P_2RhS$
Molecular weight	858.58
Crystal habit	orange plate
Crystal dimensions [mm]	0.22 × 0.08 × 0.06
Crystal system	orthorhombic
Space group	*P*212121
a [Å]	11.9840(10)
b [Å]	17.1000(10)
c [Å]	18.8990(10)
α [°]	90.00
β [°]	90.00
γ [°]	90.00
V [Å^3]	3872.9(4)
Z	4
d [g-cm^{-3}]	1.472
*F*000	1784
μ [cm^{-1}]	0.986
Absorption corrections	multiple scans; 0.8123 min, 0.9432 max
Diffractometer	KappaCCD
X-ray source	Mo-K_α
λ [Å]	0.71069
Monochromator	graphite
T [K]	150.0(10)
Scan mode	phi and omega scans
Maximum θ	30.03
hkl ranges	−16 16; −23 23; −26 26
Reflections measured	11222
Unique data	11222
Rint	0.0000
Reflections used	10128
Criterion	> 2σ(*I*)
Refinement type	Fsqd
Hydrogen atoms	mixed
Parameters refined	382
Reflections/parameter	26
wR	20.1184
*R*1	0.0416
Flack's parameter	0.050(18)
Weights *a*, *b*	0.0702; 1.9976
GoF	1.040
difference peak/hole [e·Å^{-3}]	0.825(0.104)/−0.546(0.104)

The same experimental procedure was applied to the hydrogenation reactions reported in Table 5. The preformed rhodium complexes **3a** and **3c** were used as the catalysts. Experiments were carried out at a 1 mmol scale, with a catalyst:substrate ratio of 5·10^{-3}.

Synthesis of the [Cl(CO)RhL_2] Complexes 7: 2,4-Dimethyl-1-ferrocenylphosphetane,[18] 2,4-dimethyl-1-phenylphosphetane,[19] and 2,5-dimethyl-1-phenylphospholane[20] were prepared as described previously. The rhodium complex [$ClRh(CO)_2]_2$ (20 mg, 5·10^{-2} mmol) and the phosphetane (or phospholane) ligand (20·10^{-2} mmol) were allowed to react in CH_2Cl_2 (2 mL) at room temperature for 15 min. ^{31}P NMR analysis of the crude reaction mixture in C_6D_6 showed quantitative formation of a single rhodium-phosphane complex. Complexes **7a**−**c** were characterised by NMR spectroscopy, without further purification. IR spectra of the crude complexes were recorded in CH_2Cl_2.

[ClRh(CO)(2,4-Dimethyl-1-ferrocenylphosphetane)] (7a): ^{31}P NMR (C_6D_6): δ = 63.6 (d, $J_{P\text{-}Rh}$ = 117 Hz). ^{1}H NMR (C_6D_6): δ = 5.32 (m, 1 H, CH_{Cp}), 4.38 (s, 5 H, $CH_{Cp'}$), 4.26 (m, 2 H, CH_{Cp}), 4.19 (m, 1 H, CH_{Cp}), 3.32 (m, 1 H), 2.52 (m, 1 H), 2.3−2.0 (m, 2 H), 1.69 (dt, *J* = 10.0, *J* = 7.7 Hz, CH_3), 1.15 (q, *J* = 7.8 Hz, CH_3).

^{13}C NMR (C_6D_6): δ = 188.7 (dt, J_{CRh} = 75, $J_{C,P}$ = 17 Hz, CO), 78.6 (t, J = 8.9 Hz, CH_{Cp}), 71.8 (CH_{Cp}), 71.6 (t, J = 14.1 Hz, C_{Cp}), 71.0 (C_{Cp}), 70.8 (CH_{Cp}), 69.6 ($CH_{Cp'}$), 39.5 (t, J = 5.3 Hz, CH_2), 31.3 (t, J = 18.4 Hz, PCH), 30.0 (t, J = 18.9 Hz, PCH), 20.1 (CH_3), 17.5 (CH_3) ppm.

[ClRh(CO)(2,5-Dimethyl-1-phenylphospholane)] (7b): ^{31}P NMR (C_6D_6): δ = 49.5 (d, $J_{P\text{-}Rh}$ = 123 Hz). ^1H NMR (C_6D_6): δ = 7.7 (m, 2 H), 7.2 (m, 3 H), 1.28 (dd, $^3J_{H\text{-}P}$ = 14.6, $^3J_{H,H}$ = 7.0 Hz, 3 H, CH_3), 0.75 (dd, $^3J_{H\text{-}P}$ = 16.0, $^3J_{H,H}$ = 7.2 Hz, 3 H, CH_3) ppm.

[ClRh(CO)(2,4-Dimethyl-1-phenylphosphetane)] (7c): ^{31}P NMR (C_6D_6): δ = 66.1 (d, $J_{P\text{-}Rh}$ = 116 Hz). ^1H NMR (C_6D_6): δ = 7.7 (m, 2 H), 7.1−7.2 (m, 3 H), 3.6 (m, J = 7.5 Hz, 1 H), 2.7 (m, 1 H), 2.2 (m, 1 H), 2.0 (m, 1 H), 1.61 (dt, J = 10.1, J = 7.5 Hz, CH_3), 0.88 (q, J = 7.4 Hz, CH_3) ppm.

CCDC-211829 (**2c**) and -211830 (**3c**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

[1] A. Marinetti, F. Labrue, J.-P. Genêt, *Synlett* **1999**, 1975−1977.
[2] U. Berens, M. J. Burk, A. Gerlach, W. Hems, *Angew. Chem. Int. Ed.* **2000**, *39*, 1981−1984.
[3] D. Heller, H. J. Drexler, J. You, W. Baumann, K. Drauz, H.-P. Krimmer, A. Börner, *Chem. Eur. J.* **2002**, *8*, 5196−5203.
[4] M. J. Burk, M. F. Gross, *Tetrahedron Lett.* **1994**, *35*, 9363−9366.
[5] O. M. Akotsi, K. Metera, R. D. Reid, R. McDonald, S. H. Bergens, *Chirality* **2000**, *12*, 514−521.
[6] An average value of 95.60° for the bite angle of dppf complexes has been calculated: P. Dierkes, P. W. N. M. van Leeuwen, *J. Chem. Soc., Dalton Trans.* **1999**, 1519−1529.
[7] F. Maienza, M. Wörle, P. Steffanut, A. Mezzetti, *Organometallics* **1999**, *18*, 1041−1049. U. Nettekoven, M. Widhalm, P. C. J. Kamer, P. W. N. M. van Leeuwen, K. Mereiter, M. Lutz, A. L. Spek, *Organometallics* **2000**, *19*, 2299−2309. A. R. Elasgir, F. Gassner, H. Görls, E. Dinjus, *J. Organomet. Chem.* **2000**, *597*, 139−145.
[8] *Inorg. Chem.* **1970**, *9*, 1−5.
[9] J.-P. Genêt, C. Pinel, V. Ratovelomanana-Vidal, S. Mallart, X. Pfister, L. Bischoff, M. C. Cano De Andrade, S. Darses, C. Galopin, A. Laffitte, J. A, *Tetrahedron: Asymmetry* **1994**, *5*, 675−690.
[10] M. J. Burk, T. G. P. Harper, C. S. Kalberg, *J. Am. Chem. Soc.* **1995**, *117*, 4423−4424.
[11] For recent reviews see: H. Kumobayashi, T. Miura, N. Sayo, T. Saito, X. Zhang, *Synlett* **2001**, 1055−1064. M. McCarthy, P. J. Guiry, *Tetrahedron* **2001**, *57*, 3809−3844.
[12] A. Marinetti, J.-P. Genêt, S. Jus, D. Blanc, V. Ratovelomanana-Vidal, *Chem. Eur. J.* **1999**, *5*, 1160−1165.
[13] A. Marinetti, S. Jus, J.-P. Genêt, L. Ricard, *J. Organomet. Chem.* **2001**, *624*, 162−166.
[14] A. Marinetti, S. Jus, J.-P. Genêt, *Tetrahedron Lett.* **1999**, *40*, 8365−8368.
[15] I. D. Gridnev, N. Higashi, K. Asakura, T. Imamoto, *J. Am. Chem. Soc.* **2000**, *122*, 7183−7194. I. D. Gridnev, M. Yasutake, N. Higashi, T. Imamoto, *J. Am. Chem. Soc.* **2001**, *123*, 5268−5276. S. Feldgus, C. R. Landis, *Organometallics* **2001**, *20*, 2374−2386.
[16] M. J. Burk, J. E. Feaster, W. A. Nugent, R. L. Harlow, *J. Am. Chem. Soc.* **1993**, *115*, 10125−10138.
[17] T. Imamoto, J. Watanabe, Y. Wada, H. Masuda, H. Yamada, H. Tsuruta, S. Matsukawa, K. Yamaguchi, *J. Am. Chem. Soc.* **1998**, *120*, 1635−1636.
[18] A. Marinetti, S. Jus, F. Labrue, A. Lemarchand, J.-P. Genêt, L. Ricard, *Synthesis* **2001**, 2095−2104.
[19] A. Marinetti, V. Kruger, F.-X. Buzin, *Tetrahedron Lett.* **1997**, *38*, 2947−2950.
[20] M. J. Burk, J. E. Feaster, R. L. Harlow, *Tetrahedron: Asymmetry* **1991**, *2*, 569−592.

Received January 24, 2003

