

Cyclic β -diketones — precursors of chiral 1,3-cyclohexadiene iron carbonyl complexes. Ligand exchange — (–)- $\text{PPh}_2(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})$ — new, chiral, diastereomer-separating ligand in organoiron chemistry

Andrej Boháč^{a,*}, Martina Lettrichová^a, Pavel Hrnčiar^a, Milan Hutta^b

^a Department of Organic Chemistry, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia

^b Department of Analytical Chemistry, Comenius University, Mlynská dolina, 842 15 Bratislava, Slovakia

Received 11 November 1994; in revised form 15 May 1995

Abstract

A synthesis of new, chiral tricarbonyliron complexes (**1**, **2**) from 1,3-cyclohexanedione and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) after their conversion to 1,3-diacetoxy-1,3-cyclohexadienes and complexation with $\text{Fe}_2(\text{CO})_9$ is described. Ligand-exchange reactions of complexes **1,2** with PPh_3 (**A**), (–)- $\text{P}(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})_3$ '(–)-TEOCEOP' (**B**) and (–)- $\text{PPh}_2(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})$ 'LACTODIPPHOS' (**C**) were accomplished in good yield. A new prospective chiral ligand for organoiron chemistry, derived from commercially available (*S*)-(–)-ethyl lactate, (–)- $\text{PPh}_2(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})$ (**C**) was found. By means of ligand **C**, a diastereoisomeric mixture of the (1,3-diacetoxy-1,3-cyclohexadiene) $\text{Fe}(\text{CO})_2\text{PPh}_2(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})$ complex **1C** (**1C**¹²⁰ and **1C**¹⁶⁰) was successfully separated.

Keywords: Cyclic β -diketones; Iron tricarbonyl; Ligand exchange; Phosphine; Phosphite; Phosphinite; Chiral ligand; Chirality; (*S*)-(–)-Ethyl lactate; NMR spectroscopy; CD spectra

1. Introduction

Recently, we have developed a method for the preparation of 1,3-diacetoxy-1,3-cycloalkadienes from five- to eight-membered ringed cyclic β -diketones [1]. The 1,3-diacetoxy-1,3-cycloalkadienes have the trapped dienol form of cyclic β -diketones and also the structure of cyclic, conjugated, prochiral dienes — convenient ligands for organoiron chemistry. 1,3-Diacetoxy-1,3-cycloalkadienes link two different areas in organic science: the chemistry of β -diketones and organoiron chemistry. In the literature, one often encounters the syntheses of complicated structures. Using ligands derived from cyclic β -diketones allows the advantages of the utilisation of a wide range of reactions from the area of β -diketone chemistry as well as reactions known in organoiron chemistry.

2. Results and discussion

Various ways of complexing conjugated cyclic dienes are known [2]. The most advantageous is considered to be thermal (41°C) complexation with $\text{Fe}_2(\text{CO})_9$. Complexation with iron pentacarbonyl requires a higher temperature [3]. The reaction of 1,3-diacetoxy-5,5-dimethyl-1,3-cyclohexadiene with $\text{Fe}(\text{CO})_5$ [4.5 equiv. $\text{Fe}(\text{CO})_5$, 143°C, 23 h, Ar, ⁿBu₂O] yielded only 43% of an expected iron(0) tricarbonyl complex **2** as the starting material decomposed during the reaction. However, under the same conditions, 1,3-cyclohexadiene has been converted to tricarbonyl(η^4 -1,3-cyclohexadiene)iron(0) in 80% yield. The optimisation of complexation with $\text{Fe}_2(\text{CO})_9$ (in terms of the quantity of reactant, the temperature and the reaction time) was examined for the six-membered cyclic conjugated dienes. The $\text{Fe}(\text{CO})_3$ complexes **1,2** prepared are racemic mixtures of enantiomers.

Various methods for the exchange of carbon monoxide during coordination with iron by phosphines or

* Corresponding author.

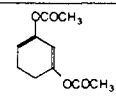
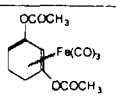
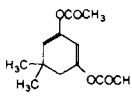
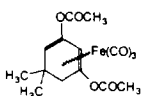
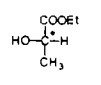
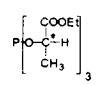
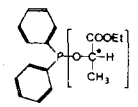
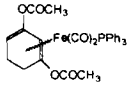
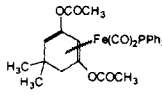
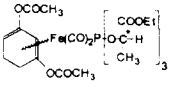
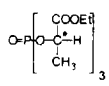
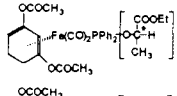
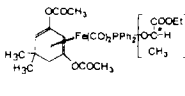
phosphites are known [4]. The most convenient ligand exchange has proved to be that of one CO by partial oxidation with Me_3NO under moderate reaction conditions [5]. Using the procedure in the literature unchanged (3 h in refluxing acetone) yielded only 40% of **1A**. The conditions were optimised (mainly, instead of refluxing acetone, by gradually increasing the reaction temperature from -78°C to $+20^\circ\text{C}$) when it was then possible to obtain excellent yields of the products (80%–99%) (**1A**, **2A**, **1C**, **2C**).

(*S*)-(-)-Ethyl lactate is readily available commercially [6]. We have synthesised (*S*),(*S*),(*S*)-(-)-tris(1-ethoxycarbonylethoxy)phosphine '(–)-TEOCEOP' (**B**) [7] and (*S*)-(-)-(1-ethoxycarbonylethoxy)diphenylphosphine 'LACTODIPPHOS' (**C**) [8] from this chiral starting material. A number of attempts to carry out the ligand exchange with Me_3NO (increasing the temperature from 0°C to $+20^\circ\text{C}$ over 4 h gave 34% **1B** + 67% **D** [9]), (increasing the temperature from -78°C to $+20^\circ\text{C}$, over 5 h gave 25%; over 24 h, 50%; over 5 d gave only 21% of **1B**) were made with only partial success. $\text{P}(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})_3$ (**B**) proved to be an unsuitable ligand. Organoiron molecules with ligand **B** were more unstable to oxidation than complexes **1,2**. Photolysis in benzene was also undertaken, but complex **1B** decomposed to the initial diene. However, (-)- $\text{PPh}_2(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})$ (**C**) was suitable as a chiral ligand. A high yield (80%) of **1C**, **2C** was observed upon ligand-exchange reaction, the products of that reaction being stable in air as were the products with PPh_3 as a ligand (**1A**, **2A**).

The new complexes (**1C**, **2C**) are mixtures of diastereoisomers. The introduction of the chiral ligand (-)- $\text{PPh}_2(\text{O}-\text{HC}^*(\text{Me})-\text{COOEt})$ (**C**) into a complex enabled the separation of the diastereoisomers (**1C**¹²⁰ and **1C**¹⁶⁰) by fractional crystallisation. The mixture may also be separated mechanically (after its crystallisation from EtOH using a magnifying lens and a tweezers — the Pasteur method [10]) because the crystals obtained are distinguishable: **1C**¹²⁰ crystallised as individual needles and **1C**¹⁶⁰ formed dendrites. Flash column chromatography separation failed because no difference in the R_f values was observed between the diastereoisomers.

The separated diastereoisomers from **1C** were characterised by their m.p., microanalysis, $[\alpha]_{546}$ (20°C), ^1H , ^{13}C NMR (with APT, INEPTL techniques), 2D NMR, CD and UV spectra. X-Ray analysis and a determination of the absolute configuration of both are under way [11]. The product **2C**, prepared from complex **2** by ligand-exchange reaction with **C**, did not crystallise. In the ^1H NMR spectra of complexes possessing Ph groups (**1A**, **2A**, **1C**, **2C**), the chemical shift ($=\text{CH}-$) ($\delta 5.40$ and $\delta 2.05$ ppm) decreased on average more than 1δ , in comparison with η^4 -(1,3-diene)Fe

Table 1
Complexations and ligand-exchange reactions

Entry	Substrate	Reaction conditions	Product / yield
1		2.5 eq. Fe_2CO_9 , 41°C , 4.5 h, C_6H_6 , Ar	 1 (75%)
2		ditto	 2 (80%)
3	 pure (<i>S</i>)-(-) isomer	0.33 eq. PCl_3 , $\text{Et}_2\text{N-Ph}$, 0°C - ($+20^\circ\text{C}$), Ar, petroleum ether	 "(-)-TEOCEOP" B (86%)
4	ditto	PPh_2Cl , $\text{Et}_2\text{N-Ph}$, 0°C - ($+20^\circ\text{C}$), Ar, petroleum ether	 "LACTODIPPHOS" C (59%)
5	1	1.1 eq. PPh_3 (A), 3.8 eq. Me_3NO , -78°C - ($+20^\circ\text{C}$), 24 h, Ar, acetone	 1A (80%)
6	2	1.1 eq. PPh_3 (A), 3.8 eq. Me_3NO , -78°C - ($+20^\circ\text{C}$), 24 h, Ar, acetone	 2A (99%)
7	1	1.1 eq. (B), 3.8 eq. Me_3NO , -78°C - ($+20^\circ\text{C}$), 24 h, Ar, acetone	 1B (50%) and  D (traces)
8	1	1.1 eq. (C), 3.8 eq. Me_3NO , -78°C - ($+20^\circ\text{C}$), 16 h, Ar, acetone	 1C (1C ¹²⁰ + 1C ¹⁶⁰)(80%)
9	2	ditto	 2C (80%)

(CO)₃ (**1**, **2**) and η^4 -(1,3-diene)Fe(CO)₂P(O-HC*(Me)-COOEt)₃ (**1B**) (δ 5.60 and δ 3.20 ppm), the shift occurring in the absorption area of the methylene hydrogens. The presence of a P atom in these molecules caused a more complex splitting of the hydrogen signals in the ¹H NMR spectra. Phosphorus also splits some of the carbon signals into doublets in the ¹³C NMR spectra.

The reactions studied are depicted schematically in Fig. 1.

3. Experimental details

3.1. General

1,3-Diacetoxy-1,3-cyclohexadiene and 1,3-diacetoxy-5,5-dimethyl-1,3-cyclohexadiene were prepared from the corresponding β -diketones by treatment with ketene in the presence of *p*-toluenesulphonic acid at elevated temperature [1]. Me₃NO [12], and also Fe₂(CO)₉ [13], were synthesised according to the published procedures. Fe(CO)₅ and PPh₃ are commercially available. All the reactions with iron and phosphorus compounds were carried out under an Ar atmosphere [14]. The reaction apparatus was purged with argon prior to use. Benzene was dried over sodium and redistilled under argon from sodium benzophenone ketyl. Petroleum ether and diethyl ether were dried over and distilled from CaH₂ under nitrogen. Acetone was dried over CaCl₂ and redistilled under argon. Solvents were purged of air by bubbling argon through the solvent for 15 min. TLC was carried out on silica gel and spots were detected by UV (λ = 254 nm) light or in iodine vapour. Flash liquid

chromatography [15] was done on SiO₂ (40/100 mesh) with (petroleum ether/ethyl acetate) as eluent. The [α]₅₄₆ (20°C) values were measured on a Polamat-A apparatus at Hg (546.1 nm) light. ¹H and ¹³C NMR spectra were measured on Varian VXR-300 (299.93 MHz and 75.43 MHz) and Tesla BS-587 (80.0 MHz and 20.1 MHz) spectrometers in CDCl₃. TMS was used as internal standard.

The APT and INEPTL techniques were applied for the exact assignment of the carbon chemical shifts. In the case of **1C**, 2D NMR, CD and UV spectra were also measured. All CD spectra were taken between 260 and 400 nm using a Dichrographe III instrument. Methanol was used as solvent and data collected at room temperature. The CD spectra of the complexes **1C**¹²⁰ (c = 1.975 mg ml⁻¹), **1C**¹⁶⁰ (c = 2.012 mg ml⁻¹) and the phosphine **C** (c = 1.401 mg ml⁻¹) are depicted in Fig. 2. The CD spectra of the diastereomeric pair [(+)-**1C**¹⁶⁰ and (-)-**1C**¹²⁰] (both of which contain LACTODIPHOS as a ligand) appear to be mirror images. The CD spectra were measured because of the known relation between the absolute configuration and the CD spectrum for related compounds (the X-ray spectra of **1C**¹²⁰ and **1C**¹⁶⁰ are to be measured). Knowledge of the absolute configuration of optically active diene-metal complexes often allows one to predict the configuration of newly created chiral centres, due to the strong stereo-directing action of the metal [16].

Gradient HPLC was used to determine the molar mass ratio of diastereomers **1C**¹²⁰ and **1C**¹⁶⁰ in the crude reaction mixture. A stainless steel column (250 × 4 mm) filled with Silasorb Phenyl sorbent (5 μ m) (Lachema Brno, Czech Republic) was used for the separation of the diastereomers. A linear gradient (30

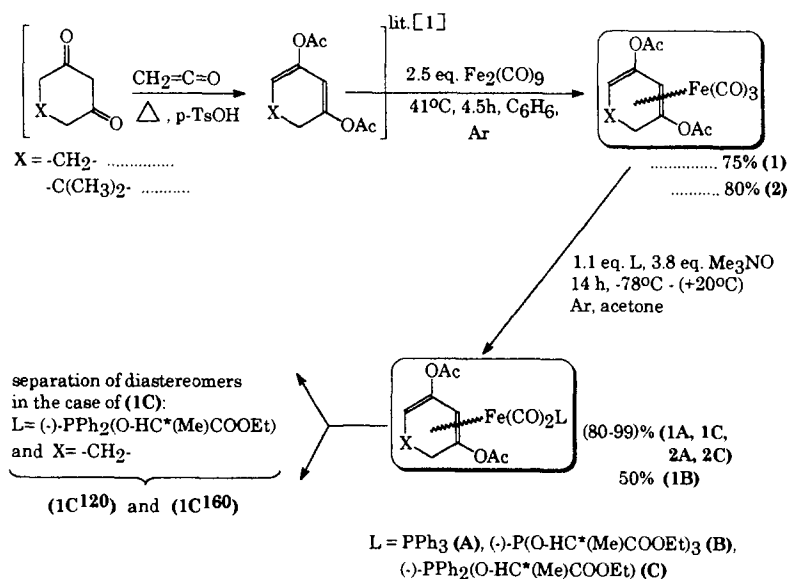


Fig. 1. Reaction summary.

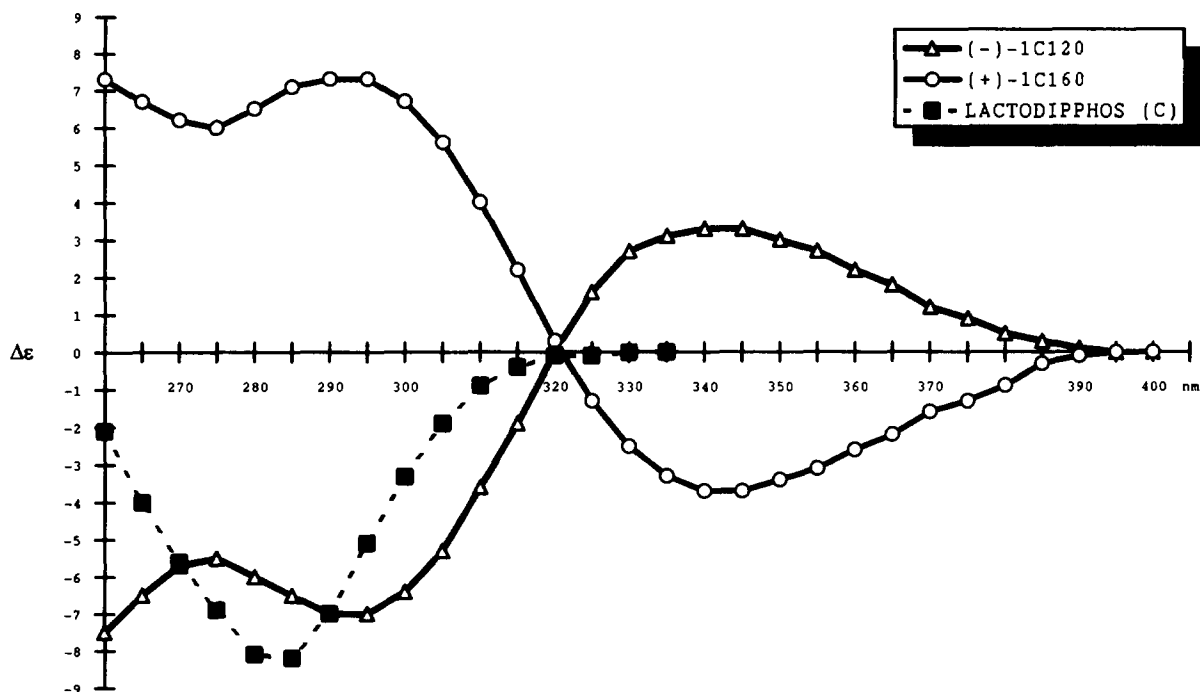


Fig. 2. CD spectra of $(-)-1C^{120}$, $(+)-1C^{160}$ (by attenuation of signals 5×10^{-5}) and Lactodipphos (C) (by 5×10^{-6}) in CH_3OH at room temperature.

min duration) of the mobile phase containing $CH_3CN/H_2O/(S)-(-)$ -ethyl lactate from 49.5 : 50.0 : 0.5% (v/v) to 99.5 : 0.0 : 0.5% (v/v) was used. The flow rate was 0.5 ml min^{-1} and 330 nm wavelength was used for the detection of signals. The UV spectra of $1C^{120}$ and $1C^{160}$ were measured on a HP-8452A Diode Array spectrophotometer in CH_3CN .

3.2. General method for the preparation of tricarbonyl $(\eta^4-1,3\text{-diacetoxy-1,3-cyclohexadiene})\text{iron}(0)$ complexes (1, 2)

A mixture of 52.0 mmol of $Fe_2(CO)_9$ and 20.8 mmol of 1,3-diacetoxy-1,3-cyclohexadiene in 45 ml of dry, oxygen-free benzene was stirred electromagnetically over 4.5 h at 41°C in a 50 ml flame-dried double-jacketed, cylindrical flask filled with argon and equipped with a septum. The reaction temperature (41°C) was kept constant by means of a thermostat which circulated warm water through the jacket of the reaction flask. The reaction was monitored by TLC on SiO_2 and detected with UV ($\lambda = 254 \text{ nm}$) light. After reaction, the mixture was filtered through Celite, concentrated on a rotary vacuum evaporator and the crude mixture subsequently purified by flash column chromatography on silica gel with argon-degassed petroleum ether/ethyl acetate as eluent (5:1 v/v). A small amount of the dark green product formed by complexation was $Fe_3(CO)_{12}$. Complexes 1 or 2 may be distilled or sublimed under low pressure using a Büchi KGR apparatus.

3.2.1. Tricarbonyl $(\eta^4-1,3\text{-diacetoxy-1,3-cyclohexadiene})\text{iron}(0)$ (1)

A yield of 5.2 g (15.5 mmol, 75%) of 1, m.p. $25\text{--}29^\circ\text{C}$ (after distillation using the Büchi KGR, $125\text{--}135^\circ\text{C}/13 \text{ Pa}$, crystallising only after storage for several weeks in a freezer) was isolated. For $C_{13}H_{12}FeO_7$, M.W. 336.08: Analysis: Found: C, 46.32; H, 3.55%. Calc. C, 46.46; H 3.60%. R_f (petroleum ether/ethyl acetate, 5:1) = 0.51. $^1\text{H NMR}$ δ : 1.50–1.80 (m, 2H, $-\text{CH}_2-$); 2.10 (m, 2H, $-\text{CH}_2-$); 2.06, 2.18 ($2 \times$ s, 6H, $2 \times \text{CH}_3\text{CO}-$); 3.30, 5.67 (m and s, respectively, 2H, $2 \times =\text{CH}-$) ppm. $^{13}\text{C NMR}$ δ : 20.83, 21.06 ($2 \times \text{CH}_3-$); 23.62, 26.28 ($2 \times -\text{CH}_2-$); 56.81, 75.02 ($2 \times =\text{CH}-$); 94.84, 123.46 [$2 \times =\text{C}(-)-$]; 168.84, 169.44 ($2 \times \text{C}=\text{O}$ from acetyl); 215.18 [$3 \times \text{C}=\text{O}$ from $Fe(CO)_3$] ppm.

3.2.2. Tricarbonyl $(\eta^4-1,3\text{-diacetoxy-5,5-dimethyl-1,3-cyclohexadiene})\text{iron}(0)$ (2)

A yield of 6.1 g (16.6 mmol, 80%) of 2, m.p. $60.0\text{--}61.5^\circ\text{C}$ [after crystallisation from petroleum ether (0.3 g ml^{-1}) and sublimation using the Büchi KGR, $100^\circ\text{C}/13 \text{ Pa}$] was isolated. For $C_{15}H_{16}FeO_7$, M.W. 364.13. Analysis: Found: C, 49.40; H, 4.38%. Calc. C, 49.48; H, 4.43%. R_f (petroleum ether/ethyl acetate, 5:1) = 0.58. $^1\text{H NMR}$ δ : 1.14 [s, 6H, $(\text{CH}_3)_2\text{C}(-)-$]; 1.66 (d, $J = 13.9 \text{ Hz}$, 1H, $-\text{CH}_2-$) (diastereotopic signal); 2.04 (s, 3H, $\text{CH}_3\text{CO}-$); 2.09 (d, $J = 13.9 \text{ Hz}$, 1H, $-\text{CH}_2-$) (diastereotopic signal); 2.18 (s, 3H, $\text{CH}_3\text{CO}-$); 3.04, and 5.80 (d, $J = 2.2 \text{ Hz}$, and m, respectively, 2H,

$2 \times =\text{CH}-$) ppm. ^{13}C NMR δ : 20.41, 20.59 ($2 \times \text{CH}_3-$ from acetyl); 30.72, 34.61 ($2 \times \text{CH}_3-$); 35.75 (quater. C); 45.17 ($-\text{CH}_2-$); 68.90, 77.25 ($2 \times =\text{CH}-$); 94.27, 122.53 [$2 \times =\text{C}(-)-$]; 168.39, 168.60 ($2 \times \text{C}=\text{O}$ from acetyl); 210.71 [$3 \times \text{C}=\text{O}$ from $\text{Fe}(\text{CO})_3$] ppm.

3.3. (S),(S),(S)-(-)-Tris(1-ethoxycarbonylethoxy)phosphine (B) '(-)-TEOCEOP' [7]

A mixture consisting of 106.7 ml (111.2 g, 0.94 mol) of (S)-(-)-ethyl lactate, 150 ml (140.7 g, 0.94 mol) of Et_2NPh (freshly distilled) and 400 ml of dry petroleum ether was cooled in an ice bath in a 1 l dry round-bottomed flask with an N_2 atmosphere equipped with a condenser, stirrer, dropping funnel and calcium chloride drying tube. A solution consisting of 27.4 ml (43.1 g, 0.31 mol) of PCl_3 (freshly distilled) in 125 ml of dry petroleum ether was dropped into the reaction mixture. The reaction mixture was then stirred for an additional 2 h at room temperature. The resulting suspension was filtered and the precipitate washed with 3×100 ml of petroleum ether and 1×50 ml of dry diethyl ether. The combined filtrates were concentrated on the rotary vacuum evaporator. The crude oil was purified by distillation; b.p. 147–149°C/67 Pa, giving 102.9 g (0.27 mol, 86.8%) of **B**, $[\alpha]_{546}^{24^\circ\text{C}} = -275.0^\circ$ (neat), R_f (petroleum ether/ethyl acetate, 2:1) = 0.54. For $\text{C}_{15}\text{H}_{27}\text{O}_9\text{P}$, M.W. 382.35. Analysis: Found: C, 46.83; H, 7.00%. Calc.: C, 47.12; H, 7.12%. ^1H NMR δ : 1.28 (t, J 7.1 Hz, 9H, $3 \times \text{CH}_3-$); 1.49 (d, J = 6.8 Hz, 9H, $3 \times \text{CH}_3-$); 4.19 (q, J = 7.1 Hz, 6H, $3 \times -\text{CH}_2\text{O}-$); 4.80 [dq, $J_{\text{HH}} = 6.8$ Hz, $J_{\text{PH}} = 9.0$ Hz, 3H, $3 \times -\text{C}^*(-)\text{H}-$] ppm.

3.4. (S)-(-)-(1-Ethoxycarbonylethoxy)diphenylphosphine (C) 'LACTODIPPHOS' [8]

A mixture consisting of 5.9 g (5.7 ml, 0.05 mol) of (S)-(-)-ethyl lactate and 7.5 g (8.0 ml, 0.05 mol) of Et_2NPh (freshly distilled) in 50 ml of dry Et_2O in a 100 ml round-bottomed flask equipped with a stirrer and a dropping funnel was cooled under an Ar atmosphere at -21°C . Then 11.0 g (9.2 ml, 0.05 mol) of Ph_2PCl was added dropwise (over 30 min) to the mixture. The reaction was stirred overnight while the temperature was increasing to room temperature. The pH was then adjusted to 7 by addition of Et_2NPh . The resulting precipitate was filtered and the solution concentrated on a rotary vacuum evaporator. The crude product was distilled. Yield, 8.9 g (0.03 mol, 59%) of **C**, b.p. 165–167°C/333 Pa, $[\alpha]_{546}^{24^\circ\text{C}} = -32.8^\circ$ (neat) [17] (for CD spectrum see Fig. 2), R_f (petroleum ether/ethyl acetate 2:1) = 0.86. For $\text{C}_{17}\text{H}_{19}\text{O}_3\text{P}$, M.W. 302.31. Analysis: Found: C, 67.33; H, 5.99. Calc.: C, 67.54; H, 6.33%. ^1H NMR δ : 1.81 (t, J = 7.1 Hz, 3H, CH_3-); 1.53 (d, J = 6.8 Hz, 3H, CH_3-); 4.13 (q, J = 7.1 Hz,

2H , $-\text{CH}_2\text{O}-$); 4.51 [dq, $J_{\text{HH}} = 7.0$ Hz, $J_{\text{PH}} = 9.4$ Hz, 1H, $-\text{C}^*(-)\text{H}-$]; 7.11–7.72 (m, 10H, PPh_2-) ppm. ^{13}C NMR δ : 13.64 (CH_3- from ester); 19.47 (d, $J_{\text{CP}} = 6.7$, CH_3- from lactic acid); 60.52 ($-\text{CH}_2\text{O}-$); 74.56 [d, $J_{\text{CP}} = 23.3$, $-\text{C}^*(-)\text{H}-$]; 127.66, 127.98 ($2 \times$ d, $J_{\text{CP}} = 3.8$ Hz each, *m* from PPh_2-); 128.74, 129.03 (*p* from PPh_2-); 129.52, 130.61 ($2 \times$ d, $J_{\text{CP}} = 1.5$ Hz and $J_{\text{CP}} = 2.3$ Hz, respectively, *o* from PPh_2-); 141.12, 141.94 ($2 \times$ d, $J_{\text{CP}} = 6.1$ Hz and $J_{\text{CP}} = 9.0$ Hz, respectively, *ipso* from PPh_2-); 171.88 (d, $J_{\text{CP}} = 4.4$ Hz, $\text{C}=\text{O}$) ppm.

3.5. General method for the ligand exchange of tricarbonyl(η^4 -1,3-cyclohexadiene) iron(0) complexes (1, 2). The synthesis of 1A, 2A, 1B, 1C and 2C

A reaction mixture consisting of 1.79 mmol of complexes **1** or **2**, 1.9 mmol of phosphine A–C and 20 ml of dry, degassed acetone in a 50 ml flask with an Ar atmosphere was cooled to -78°C . Then 0.5 g (6.8 mmol) of $(\text{CH}_3)_3\text{NO}$ was added and the reaction mixture stirred overnight. The temperature was allowed to increase to room temperature. After reaction, the mixture was carefully filtered through Celite 545 [18]. The filtrate was concentrated on the rotary vacuum evaporator and the crude product purified by flash chromatography yielding a yellow, foamy solid, or brown oil. The product could be crystallised from a mixture of ethyl acetate/hexane, or from EtOH.

3.5.1. Dicarbonyl(η^4 -1,3-diacetoxy-1,3-cyclohexadiene)(triphenylphosphine) iron(0) (1A)

A yield of 0.8 g (1.43 mmol, 80%) of **1A**, m.p. 154–160°C (from ethyl acetate/hexane), R_f (petroleum ether/ethyl acetate, 2:1) = 0.56, was isolated. For $\text{C}_{30}\text{H}_{27}\text{FeO}_6\text{P}$, M.W. 570.36. Analysis: Found: C, 63.08; H, 4.37%. Calc.: C, 63.18; H, 4.77%. ^1H NMR δ : 1.50–1.87 (m, 3H, $=\text{CH}-$, $-\text{CH}_2-$); 1.62 (s, 3H, $\text{CH}_3\text{CO}-$); 2.00–2.40 (m, 2H, $-\text{CH}_2-$); 2.07 (s, 3H, $\text{CH}_3\text{CO}-$); 5.49 (s, 1H, $=\text{CH}-$); 7.30–7.50 (m, 15H, PPh_3) ppm. ^{13}C NMR δ : 20.57, 21.43 ($2 \times \text{CH}_3-$); 23.83 (d, $J_{\text{CP}} = 6.8$ Hz, $-\text{CH}_2-$); 27.71 ($-\text{CH}_2-$); 59.78 (d, $J_{\text{CP}} = 3.8$ Hz, $=\text{CH}-$); 72.12 ($=\text{CH}-$); 92.15 [d, $J_{\text{CP}} = 12.1$ Hz, $=\text{C}(-)-$]; 122.5 (*ipso*- PPh_3); 128.06 (d, $J_{\text{CP}} = 9.1$ Hz, *m*- PPh_3); 129.76 (*p*- PPh_3); 133.52 (d, $J_{\text{CP}} = 11.3$ Hz, *o*- PPh_3); 134.89 [d, $J_{\text{CP}} = 38.5$ Hz, $=\text{C}(-)-$]; 169.70, 169.87 ($2 \times \text{C}=\text{O}$ from acetyl); 215.46, 219.25 [$2 \times \text{C}=\text{O}$ from $\text{Fe}(\text{CO})_2$] ppm.

3.5.2. Dicarbonyl(η^4 -1,3-diacetoxy-5,5-dimethyl-1,3-cyclohexadiene)(triphenylphosphine)iron(0) (2A)

A yield of 1.06 g (1.77 mmol, 99%) of **2A**, m.p. 182–186°C (from ethyl acetate/hexane), R_f (petroleum ether/ethyl acetate, 2:1) = 0.60, was isolated. For $\text{C}_{32}\text{H}_{31}\text{FeO}_6\text{P}$, M.W. 598.42. Analysis: Found: C, 64.12; H, 5.15%. Calc.: C, 64.23; H, 5.22%. ^1H NMR δ : 0.91, 1.02 [$2 \times$ s, 6H, $(\text{CH}_3)_2\text{C}(-)-$]; 1.60 (s, 3H,

CH₃CO-); 1.62–1.80 (m, 2H, -CH₂-); 2.05 (s, 3H, CH₃CO-); 2.23 (m, 1H, =CH-); 5.62 (s, 1H, =CH-); 7.25–7.62 (m, 15H, PPh₃) ppm. ¹³C NMR δ: 20.74, 21.39 (2 × CH₃- from acetyl); 30.65, 34.51 (2 × CH₃-); 35.74 (d, *J*_{CP} = 4.5 Hz, quater. C); 46.10 (-CH₂-); 72.84 (d, *J*_{CP} = 3.8 Hz, =CH-); 73.58 (=CH-); 90.55 [d, *J*_{CP} = 12.1 Hz, =C(-)]; 120.99 (*ipso*-PPh₃); 128.00 (d, *J*_{CP} = 9.1 Hz, *m*-PPh₃); 129.78 (*p*-PPh₃); 133.61 (d, *J*_{CP} = 10.6 Hz, *o*-PPh₃); 134.78 [d, *J*_{CP} = 39.2 Hz, =C(-)]; 169.22, 169.51 (2 × C=O from acetyl); 215.87, 220.05 [2 × d, *J*_{CP} = 21.9 Hz and *J*_{CP} = 3.8 Hz, respectively, 2 × C=O from Fe(CO)₂] ppm.

3.5.3. Dicarboxyl(η⁴-1,3-diacetoxy-1,3-cyclohexadiene)[(S),(S),(S)-tris(1-ethoxycarbonylethoxy)phosphine] iron(0) (1B)

A yield of 0.62 g (0.89 mmol, 50%) of **1B**, *R*_f (petroleum ether/ethyl acetate, 2:1) = 0.37 (mixture of diastereomers) was isolated. For C₂₇H₃₉FeO₁₅P M.W. 690.42. Analysis: Found: C, 46.82; H, 5.43%. Calc.: C, 46.97; H, 5.69%. ¹H NMR δ: 0.87–1.90 (m, 4H, 2 × -CH₂-); 1.27 (t, *J* = 7.1 Hz, 9H, 3 × CH₃-); 1.53 (d, *J* = 6.8 Hz, 9H, 3 × CH₃-); 2.05 (s, 3H, CH₃CO-); 2.08 (s, 3H, CH₃CO-); 3.20–3.36 (m, 1H, =CH-); 4.16 (q, *J* = 7.1 Hz, 6H, 3 × -CH₂-O-); 4.92 [dq, *J*_{HH} = 6.8 Hz, *J*_{PH} = 11.2 Hz, 3H, 3 × -C*(-)H-]; 5.36 (m, 1H, =CH-) ppm.

Triethyl O, O', O''-phosphoryltri(L-lactate) (D) [9]

A yield of 67% of **D** (as a by-product in the synthesis of **1B** (yield of 34% by utilising the temperature from 0°C to +20°C over 4 h, acetone), *R*_f (petroleum ether/ethyl acetate 2:1) = 0.15, was isolated. For C₁₅H₂₇O₁₀P, M.W. 398.35. Analysis: Found: C, 44.98; H, 6.66%. Calc.: C, 45.23; H, 6.83%. ¹H NMR δ: 1.29 (t, *J* = 7.1 Hz, 9H, 3 × CH₃-); 1.59 (d, *J* = 6.8 Hz, 9H, 3 × CH₃-); 4.22 (q, *J* = 7.1 Hz, 6H, 3 × -CH₂-O-); 5.02 [dq, *J*_{HH} = 6.8 Hz, *J*_{PH} = 7.0 Hz, 3H, 3 × -C*(-)H-] ppm.

3.5.4. Dicarboxyl(η⁴-1,3-diacetoxy-1,3-cyclohexadiene)[(S)-(1-ethoxycarbonylethoxy)diphenylphosphine] iron(0) (1C)

A yield of 0.87 g (1.43 mmol, 80%) of **1C** (= **1C**¹²⁰ + **1C**¹⁶⁰), (for CD spectra see Fig. 2), *R*_f (petroleum ether/ethyl acetate, 2:1) = 0.62 (mixture of diastereomers), was isolated. C₂₉H₃₁FeO₉P, M.W. 610.38. Upon crystallisation of the mixture (**1C**¹²⁰ + **1C**¹⁶⁰) from EtOH, the isomer **1C**¹⁶⁰ crystallised first. Both of the diastereomers are yellow crystalline compounds. The molar mass ratio of the diastereomers (**1C**¹⁶⁰)/(**1C**¹²⁰) was 1.40 the (diastereomer excess of 16.7% was determined by gradient HPLC from the crude reaction mixture).

(+)-Dicarboxyl(η⁴-1,3-diacetoxy-1,3-cyclohexadiene)-[(S)-(1-ethoxycarbonylethoxy)diphenylphosphine] iron(0) (1C¹⁶⁰)

1C¹⁶⁰, m.p. 160–162°C (from EtOH), [α]₅₄₆ (20°C) = +53.68° (*c* = 0.93 g 100 ml⁻¹; EtOH), was isolated. For C₂₉H₃₁FeO₉P, M.W. 610.38. Analysis: Found: C, 56.85; H, 4.99%. Calc.: C, 57.07; H, 5.12%. UV (CH₃CN): λ_{max} = 300 nm, log ε = 2.66 m² mol⁻¹. ¹H NMR δ: 1.02 (t, *J* = 7.17 Hz, 3H, CH₃-); 1.49 (d, *J* = 6.87 Hz, 3H, CH₃-); 1.50–1.80 (m, 3H, -CH₂- and one diastereotopic from -CH₂- of diene); 1.97, 2.06 (2 × s, 6H, 2 × CH₃CO-); 2.02–2.09 (m, 1H, =CH-); 2.12–2.26 (m, 1H, diastereotopic from -CH₂- of diene); 3.92 (q, *J* = 7.20 Hz, 2H, -CH₂O-); 4.72 [dq, *J*_{HH} = 6.74 Hz, *J*_{PH} = 11.17 Hz, 1H, -C*(-)H-]; 5.16 (s, 1H, -CH=); 7.38 (m, 6H, *m* and *p* from PPh₂-); 7.45–7.60, 7.60–7.72 (2 × m, 4H, *o* from PPh₂-) ppm. ¹³C NMR δ: 13.72 (CH₃- from ethyl ester); 19.74 (d, *J*_{CP} = 4.5 Hz, CH₃- from lactic acid); 20.88, 21.36 (2 × CH₃- from acetyl); 23.86 (d, *J*_{CP} = 6.8 Hz, -CH₂-); 27.34 (-CH₂-); 60.33 (d, *J*_{CP} = 3.0 Hz, =CH-); 61.11 (-CH₂O-); 71.73 [-C*(-)H-]; 72.21 (=CH-); 93.05 [d, *J*_{CP} = 13.6 Hz, =C(-)]; 122.57 [=C(-)]; 127.90 (d, *J*_{CP} = 9.8 Hz, *m* from PPh₂-); 130.16, 130.37 (2 × s, *p* from PPh₂-); 131.00, 131.80 (2 × d, *J*_{CP} = 12.8 Hz and *J*_{CP} = 12.1 Hz, respectively, *o* from PPh₂-); 139.07, 139.67 (2 × d, *J*_{CP} = 21.9 Hz and *J*_{CP} = 22.6 Hz, respectively, *ipso* from PPh₂-); 169.58, 170.14 (2 × C=O from acetyl); 172.20 (d, *J*_{CP} = 71.7 Hz, C=O from ethyl ester); 214.32, 218.86 [2 × d, *J*_{CP} = 24.1 Hz and *J*_{CP} = 3.8 Hz, respectively, 2 × C=O from Fe(CO)₂] ppm.

(-)-Dicarboxyl(η⁴-1,3-diacetoxy-1,3-cyclohexadiene)-[(S)-(1-ethoxycarbonylethoxy)diphenylphosphine] iron(0) (1C¹²⁰)

1C¹²⁰, m.p. 121–123°C (from EtOH), [α]₅₄₆ (20°C) = -128.54° (*c* = 1 g 100 ml⁻¹, EtOH), was isolated. For C₂₉H₃₁FeO₉P, M.W. 610.38. Analysis: Found: C, 56.98; H, 5.03%. Calc.: C, 57.07; H, 5.12%. UV (CH₃CN): λ_{max} = 300 nm, log ε = 2.74 m² mol⁻¹. ¹H NMR δ: 1.23 (d, *J* = 6.72 Hz, 3H, CH₃-); 1.28 (t, *J* = 7.14 Hz, 3H, CH₃-); 1.55–1.79 (m, 3H, -CH₂- and one diastereotopic from -CH₂- of diene); 1.92–2.05 (m, 1H, =CH-); 1.98, 2.10 (2 × s, 6H, 2 × CH₃CO-); 2.18–2.32 (m, 1H, diastereotopic from -CH₂- of diene); 4.13, 4.22 (2 × dq, *J*_{HH} = 10.7 Hz, *J*_{HH} = 7.19 Hz each, 2H, diastereotopic from -CH₂O-); 4.80 [dq, *J*_{HH} = 6.72 Hz, *J*_{PH} = 10.2 Hz, 1H, -C*(-)H-]; 5.28 (s, 1H, =CH-); 7.30–7.44 (m, 6H, *m* and *p* from PPh₂-); 7.55–7.64, 7.75–7.85 (2 × m, 4H, *o* from PPh₂-) ppm. ¹³C NMR δ: 14.23 (CH₃- from ethyl ester); 20.07 (CH₃- from lactic acid); 20.72, 21.42 (2 × CH₃- from acetyl); 23.87 (d, *J*_{CP} = 7.5 Hz, -CH₂- from diene); 27.34 (-CH₂- from diene); 61.02 (-CH₂O-); 61.16 (d, *J*_{CP} = 3.8 Hz, =CH-); 71.79 (=CH-); 71.98 [d, *J*_{CP} = 3.8 Hz, -C*(-)H-]; 93.04 [d, *J*_{CP} = 15.1 Hz, =C(-)]; 122.70 [=C(-)]; 127.92, 128.12 (2 × d, *J*_{CP} = 9.8 Hz, *J*_{CP} = 10.6 Hz, respectively, *m* from PPh₂-); 129.79 (*p* from PPh₂-); 130.44

(d, $J_{CP} = 12.1$ Hz, *o* from PPh_2-); 130.65 (*p* from PPh_2-); 131.80 (d, $J_{CP} = 12.1$ Hz, *o* from PPh_2-); 139.29, 140.62 ($2 \times$ d, $J_{CP} = 49.0$ Hz and $J_{CP} = 43.7$ Hz, respectively, *ipso* from PPh_2-); 169.60, 170.70 ($2 \times$ C=O from acetyl); 171.99 (d, $J_{CP} = 9.1$ Hz, C=O from ethyl ester); 214.42 [d, $J_{CP} = 24.9$ Hz, C=O from $Fe(CO)_2$]; 219.44 [C=O from $Fe(CO)_2$] ppm.

3.5.5. Dicarbonyl(η^4 -1,3-diacetoxy-5,5-dimethyl-1,3-cyclohexadiene)[(S)-(1-ethoxycarbonylethoxy)diphenylphosphine] iron(0) (2C)

A yield of 0.92 g (1.44 mmol, 80%) of **2C**, oil, R_f (petroleum ether/ethyl acetate, 2:1) = 0.70 of a diastereomeric mixture, was isolated. For $C_{31}H_{35}FeO_9P$, M.W. 638.43. Analysis: Found: C, 58.02; H, 5.22%. Calc.: C, 58.32; H, 5.53%. 1H NMR δ : 0.62–1.04 [m, 12H, $2 \times (CH_3)_2C(-)-$]; 1.04–1.42 [m, 12H, $2 \times (CH_3-$ from ethyl ester and CH_3- from lactic acid)]; 1.42–2.50 [m, 18H, $2 \times (2 \times CH_3CO-$, $-CH_2-$ from diene and $=CH-$]; 3.77–4.27 (m, 4H, $2 \times -CH_2O-$); 4.42–4.90 [m, 2H, $2 \times -C^*(-)H-$]; 5.45 (s, 2H, $2 \times =CH-$); 7.17–7.52 [m, 12H, $2 \times (4 \times m$ and $2 \times p$ from PPh_2-); 7.52–7.90 [m, 8H, $2 \times (4 \times o$ from PPh_2-] ppm.

Acknowledgements

We thank the Drug Research Institute, Modra Slovakia for financial support of this work. Also, we would like to thank Dr. N. Pronayová from the Slovak Technical University for the measurements of the 1H , ^{13}C and 2D NMR spectra and Ing. T. Sticzay from the Chemical Institute of the Slovak Academy of Science for CD spectra.

References and notes

- [1] A. Boháč and P. Hrnčiar, *Synthesis*, (1991) 881.
- [2] G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry*, Pergamon Press, Oxford, 1982, Vol. 4, p. 434.
- [3] A.J. Birch, *J. Chem. Soc. A*, (1968) 332.
- [4] A.J. Pearson, S.L. Kole and T. Ray, *J. Am. Chem. Soc.*, 106 (1984) 6060; F.M. Chaudari and P.L. Pauson, *J. Organomet. Chem.*, 5 (1966) 73.
- [5] A.J. Birch, L.F. Kelly, *J. Organomet. Chem.*, 286 (1985) C5.
- [6] Aldrich Co., Buchs (Switzerland) Cat. No. E-3, 410-2, 1994–95, p. 701 (1-L of 98% ethyl (S)-(-)-lactate [687-47-8], 29.30 sFr).
- [7] Also triethyl O,O',O''-phosphinetriyl tri(L-lactate).
- [8] Also ethyl O-diphenylphosphino-L-lactate.
- [9] Compound **B** is sensitive to oxidation with Me_3NO at temperatures above $0^\circ C$ in acetone and the result of this reaction is triethyl O,O',O''-phosphoryl tri(L-lactate) (**D**).
- [10] H. Hart, *Organic Chemistry*, Houghton Mifflin Co., Boston, MA, 1987, p. 141.
- [11] To be published in *Acta Crystallogr.*
- [12] H. Freytag, *Houben Weyl*, Georg Thieme Verlag, Stuttgart, 1958, Vol. XI/2, p. 190.
- [13] G. Brauer, *Handbuch der Präparativen Anorganischen Chemie*, Ferdinand Enke Verlag, Stuttgart 1981, Vol. 3, p. 1827.
- [14] We developed a small apparatus 'The Transferable Gas Container (TGC)' for introducing an inert gas into a reaction mixture, a solvent or a solution. TGC attached to a syringe allows convenient degassing of liquids. A. Boháč, *J. Chem. Educ.*, 72 (1995) 263.
- [15] C.W. Still, M. Kahn and A. Mitra, *J. Org. Chem.*, 43 (1978) 2923.
- [16] (a) N. Morita, T. Asao, H. Sotokawa, M. Hatano and A. Tajiri, *J. Organomet. Chem.*, 339 (1988) C1; (b) A. Marcuzzi, A. Linden, D. Rentsch and W. Philipsborn, *J. Organomet. Chem.*, 429 (1992) 87.
- [17] $[\alpha]_{546}^{20^\circ C} = -38.8^\circ$ ($c = 10.3$; EtOH) from J. Beneš and J. Hetflejš, *Collect. Czech. Chem. Commun.*, 41 (1976) 2256.
- [18] The precipitate was very fine and caused some problems upon filtration.