Journal of Organometallic Chemistry, 429 (1992) 87–97
Elsevier Sequoia S.A., Lausanne
JOM 22457

Resolution of $[(\eta^4\text{-benzylideneacetone})\text{Fe(CO)}_3]$. Structure and configurational stability of $[(pS)\text{-(benzylideneacetone)Fe(CO)}_2\text{L}^\star]$ ($\text{L}^\star$ = (+)-neomenthyldiphenylphosphine)

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(Received September 30, 1991)

Abstract

Resolution of $[(\eta^4\text{-benzylideneacetone})\text{Fe(CO)}_3]$ has been achieved by (reversible) thermal displacement of a CO ligand by use of the chiral phosphine (+)-neomenthyldiphenylphosphine ((+)-NMDPP). The two diastereomers formed were separated by chromatography and treated with carbon-monoxide to give the corresponding optically active Fe(CO)_3 complexes. The circular dichroism spectra are discussed. The absolute configuration of the planar chirality element in the two diastereomers has been determined by an X-ray diffraction study.

Introduction

Many optically active (diene)Fe(CO)_3 complexes have been synthesized by use of classical methods, such as resolution with chiral derivatizing agents [1–5]. Enantioselective chromatographic methods were employed to resolve non-functionalized complexes [6]. Kinetic resolution of these non-functionalized complexes was also achieved by treating optically active (enone)Fe(CO)_3 complexes with prochiral dienes [7,8]; it was suggested that the asymmetric induction involves an intermediate in which enone and diene are simultaneously coordinated to the same iron atom [9,10]. However, these optically active transfer reagents were derived from chiral natural products such as (+)-pulegone and (+)-pinocarvone. We decided to try to separate the two diastereomers produced when a CO ligand is displaced from $[(\eta^4\text{-benzylideneacetone})\text{Fe(CO)}_3]$ by (+)-NMDPP. A similar separation of $[(\eta^4\text{-diene})\text{Fe(CO)}_3]$ complexes was achieved by Howell *et al.* [11] using methylsorbate, sorbinaldehyde, and 1-methoxycyclohexadiene as organic

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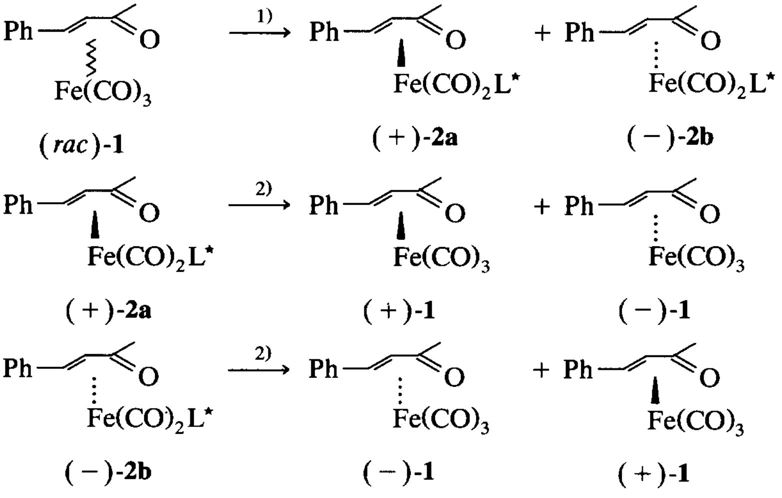
ligands. Each of the two diastereomers that we obtained was subsequently treated with CO to give the corresponding optically active [(η^4-benzylideneacetone)Fe$(CO)_3$] complexes. Our main interest was in the chiroptical properties of these complexes and in the fact that during the second step (e.g. L^*-exchange with CO) partial racemization occurs, depending on the temperature and reaction time. Complexes of this type could be useful as chiral transfer reagents.

Results and discussion

[(η^4-Benzylideneacetone)Fe$(CO)_3$] (*rac*)-**1** was synthesized as previously described [12]. The diastereomeric complexes (+)-**2a** and (−)-**2b** were prepared in high yields by treating ((*rac*)-**1**) with (+)-NMDPP [13] and trimethylamine oxide (TMNO) in acetonitrile at 25°C (Scheme 1). The ratio of the two diastereomers was approximately 1/1, and they were readily separated by column chromatography with 6/1 hexane/ether as eluent. Crystals suitable for X-ray study were obtained by dissolving (+)-**2a** in methanol and keeping the solution at −30°C for 24 h. Table 1 gives the crystallographic data and Table 2 shows selected bond distances and angles. Atomic coordinates for non-hydrogen atoms are given in Table 3. The molecular structure of (+)-**2a** is illustrated in Fig. 1. The coordination geometry of the Fe atom may be described as distorted square pyramidal. The base of the pyramid is defined by the centres of the heterodiene double bonds and the two CO ligands. The P ligand is in an apical site. With the known absolute configuration of the (+)-neomenthyldiphenyl-phosphine group the planar chirality of [(+)-(benzylideneacetone)Fe(CO_2L^*)] (L^* = (+)-NMDPP) is derived as (*pS*).

The circular dichroism spectra of (+)-**2a** and (−)-**2b** show an approximate mirror image pattern (Fig. 2). Thus, the chiral phosphine does not have a great influence on the chiroptical properties of such planar chiral substances, in agreement with earlier observations by Howell *et al.* for similar complexes [11]. Another



Scheme 1. (1) L^*, trimethylaminoxide, acetonitrile, 25°C. (2) 1 atm CO, toluene, Δ; L^* = (+)-neomenthyldiphenylphosphine ((+)-NMDPP). Ratio (+)-1/(−)-1 is dependent on the temperature and reaction time.

Table 1

Summary of crystal data

Empirical formula	$C_{34}H_{39}FeO_3P$
Molecular weight	582.49
Color, habit	orange prisms
Space group	monoclinic, $P2_1$, $Z = 2$
Unit cell dimensions	$a = 9.118(3)$, $b = 18.603(5)$,
(from 25 refl. with $28° < 2\theta < 32°$)	$c = 9.758(2)$ Å; $\beta = 115.36(2)°$
Volume	1495.7(7) Å^3
$D_{calcd.}$	1.293 g cm^{-3}
Scan speed	variable, 2.5–19.3°/min
Temperature of data collection	−60°C
Radiation	Mo-K_α (graphite-monochromated) $\lambda = 0.70926$ Å μ(Mo-K_α) = 5.860 cm^{-1}
Max. and min. absorption correction	1.090, 0.875
$F(000)$	616
Total reflections measured	4446
Unique total	3749 ($R_{int} = 0.030$)
Observed total	3305 [observed if $I > 2\sigma(I)$]
Scan range	$2\theta_{(max)} = 55°$
Least squares parameters	501
Final residuals	$R = 0.0383$, $wR = 0.0393$
w	$[\sigma^2(F)]^{-1}$
Residual electron density (eÅ^{-3})	max.: 0.51 (near P and Fe), 0.26 elsewhere, min.: −0.36

enantiomerically pure (heterodiene)Fe(CO)$_3$ complex was recently obtained in our group [14]. The corresponding CD spectrum of this (*pR*)-complex ((−)-**3**) exhibits a negative Cotton effect at long wave lengths (Fig. 3). Since we synthesized just

Table 2

Selected bond distances (Å) and bond angles (°)

P–Fe	2.274(1)	P–Fe–O(1)	98.21(9)
Fe–O(1)	2.035(3)	P–Fe–C(2)	133.5(1)
Fe–C(2)	2.039(5)	P–Fe–C(3)	129.3(1)
Fe–C(3)	2.049(4)	P–Fe–C(4)	90.5(1)
Fe–C(4)	2.152(5)	P–Fe–C(12)	104.3(2)
Fe–C(11)	1.736(5)	P–Fe–C(11)	103.3(2)
Fe–C(12)	1.768(5)	O(1)–Fe–C(2)	71.4(2)
C(12)–O(3)	1.157(6)	O(1)–Fe–C(4)	76.5(2)
C(11)–O(2)	1.162(6)	C(4)–Fe–C(11)	99.7(2)
O(1)–C(2)	1.310(6)	O(1)–Fe–C(12)	88.4(2)
C(2)–C(3)	1.421(6)	O(1)–Fe–C(3)	68.9(2)
C(3)–C(4)	1.417(6)	O(1)–Fe–C(11)	158.2(2)
C(3)–H(3)	0.95	C(2)–C(3)–H(3)	122.0
C(4)–H(4)	0.92(5)	C(3)–C(4)–H(4)	113.(3)
C(4)–C(5)	1.475(7)	Fe–P–C(29)	106.3(1)
P–C(13)	1.860(4)	Fe–P–C(13)	118.8(1)
P–C(23)	1.832(4)	Fe–P–C(23)	118.1(1)
P–C(29)	1.821(4)	C(13)–P–C(23)	105.8(2)

Table 3
Atomic coordinates

Atom	x	y	z
Fe	0.60937(6)	0.98710	0.85600(6)
P	0.8578(1)	0.95141(6)	0.8801(1)
O(1)	0.5702(4)	1.0672(2)	0.7024(3)
O(2)	0.5254(5)	0.8907(2)	1.0440(4)
O(3)	0.6710(4)	1.0994(2)	1.0837(4)
C(1)	0.3264(6)	1.1073(3)	0.7237(6)
C(2)	0.4312(5)	1.0499(2)	0.7030(5)
C(3)	0.3873(5)	0.9763(2)	0.6749(5)
C(4)	0.4953(5)	0.9328(2)	0.6411(5)
C(5)	0.4732(5)	0.8549(3)	0.6110(5)
C(6)	0.4115(7)	0.8082(3)	0.6836(6)
C(7)	0.3948(8)	0.7349(3)	0.6471(9)
C(8)	0.4372(8)	0.7085(4)	0.5380(9)
C(9)	0.4962(8)	0.7535(4)	0.4628(8)
C(10)	0.5151(6)	0.8274(3)	0.4983(7)
C(11)	0.5665(5)	0.9265(3)	0.9691(5)
C(12)	0.6522(5)	1.0537(2)	0.9973(5)
C(13)	0.8986(5)	0.8537(2)	0.8761(5)
C(14)	0.8460(5)	0.8055(2)	0.9782(5)
C(15)	0.8703(7)	0.7265(3)	0.9462(7)
C(16)	1.0365(8)	0.7084(3)	0.9548(8)
C(17)	1.0835(7)	0.7564(3)	0.8542(6)
C(18)	1.0685(6)	0.8357(3)	0.8895(6)
C(19)	0.9093(6)	0.8258(3)	1.1486(5)
C(20)	0.8254(9)	0.7810(4)	1.2233(8)
C(21)	1.0929(7)	0.8237(4)	1.2478(7)
C(22)	0.9887(9)	0.7395(4)	0.6838(8)
C(23)	1.0376(4)	0.9887(3)	1.0365(4)
C(24)	1.0322(5)	1.0053(2)	1.1739(4)
C(25)	1.1699(6)	1.0304(3)	1.2962(5)
C(26)	1.3111(6)	1.0397(3)	1.2850(5)
C(27)	1.3199(6)	1.0247(3)	1.1483(6)
C(28)	1.1828(5)	0.9994(3)	1.0267(5)
C(29)	0.8791(4)	0.9871(3)	0.7157(4)
C(30)	0.8627(6)	0.9466(3)	0.5904(5)
C(31)	0.8600(6)	0.9784(3)	0.4615(5)
C(32)	0.8761(6)	1.0526(3)	0.4561(5)
C(33)	0.8938(6)	1.0943(3)	0.5801(5)
C(34)	0.8948(5)	1.0613(3)	0.7075(5)

three optically active enone complexes of this type, it is too early to propose a general rule for predicting the corresponding Cotton effect (CE), but it seems that (*pS*)-complexes exhibit a positive and (*pR*)-complexes a negative CE at long wave lengths.

The optically active $Fe(CO)_3$ complexes (+)-**1** and (−)-**1** were made by treating the pure diastereomers ((+)-**2a** and (−)-**2b**) with CO. (A similar ligand displacement from racemic [(η^4-benzylideneacetone)$Fe(CO)_2PPh_3$] by CO to give the corresponding $Fe(CO)_3$ complex was reported several years ago [15].) We treated each diastereomerically pure $Fe(CO)_2L^*$ complex with CO in toluene at various

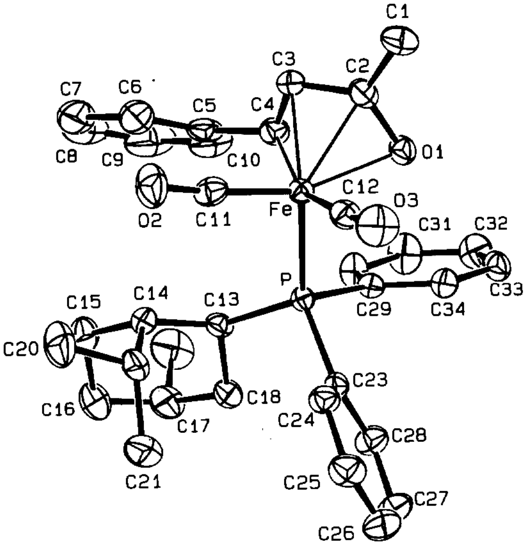


Fig. 1. Structure of [(*p*S)-(η^4-benzylideneacetone)Fe(CO)$_2$L*] (L* = (+)-NMDPP) ((+)-**2a**).

temperatures and for various times. To our great surprise we could not isolate the expected enantiomerically pure synthons (+)-**1** and (−)-**1**. Partial racemization, the extent of which depends on the temperature and time must take place during this displacement reaction with the phosphine (Scheme 1, Table 4). The ratio of the enantiomers was established by use of an NMR shift reagent (Fig. 4). On addition of 0.2 equivalents of the chiral shift reagent Eu(tfc)$_3$ the doublet of the C(4) proton signal of [(η^4-benzylideneacetone)Fe(CO)$_3$] is shifted down-field and separates into two broadened signals for each enantiomer. The more intense signal

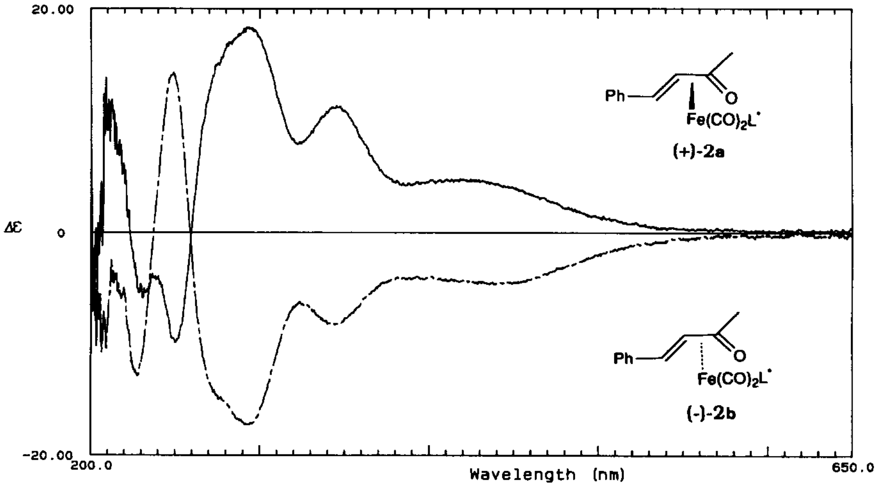


Fig. 2. CD spectra of (+)-**2a** and (−)-**2b**.

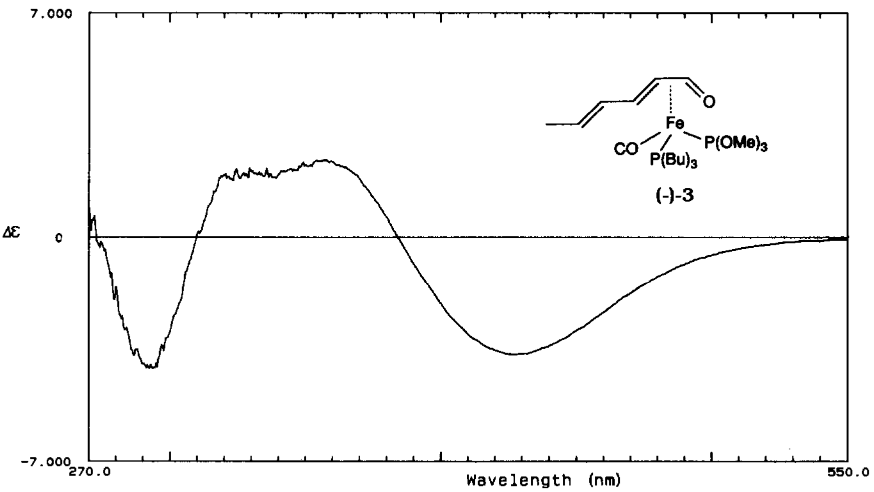


Fig. 3. CD spectrum of [(*S*, *pR*)-(sorbaldehyde)Fe(CO)PBu$_3$P(OMe)$_3$] ((−)-**3**).

Table 4

Experimental data for L*/CO exchange in (+)-**2a** (L* = (+)-NMDPP) at different temperatures

Reaction temperature (°)	Reaction time (h)	Yield (%)	Ratio (+)-**1**/(−)-**1**
25	31	50	25/1
45	2.5	67	25/2
65	2.5	89	25/3

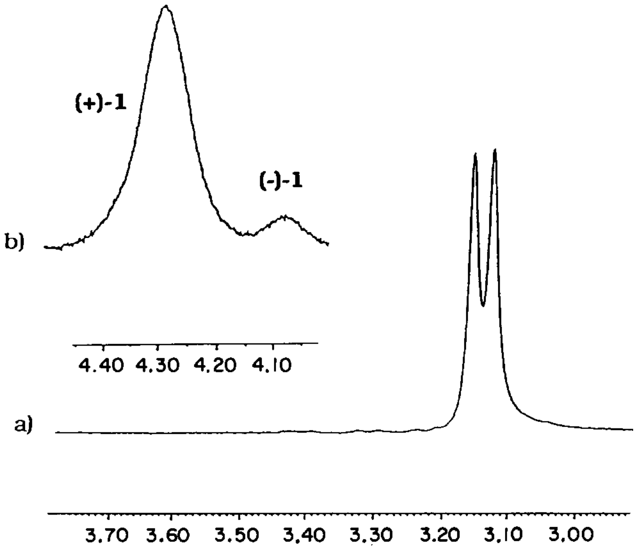


Fig. 4. ^{1}H NMR doublet of H-C(4) (300 MHz, C_6D_6) of enriched [(benzylideneacetone)Fe(CO)$_3$] ((+)-**1**/(−)-**1** = 10/1): (a) without chiral shift reagent; (b) with 0.2 eq. of Eu(tfc)$_3$.

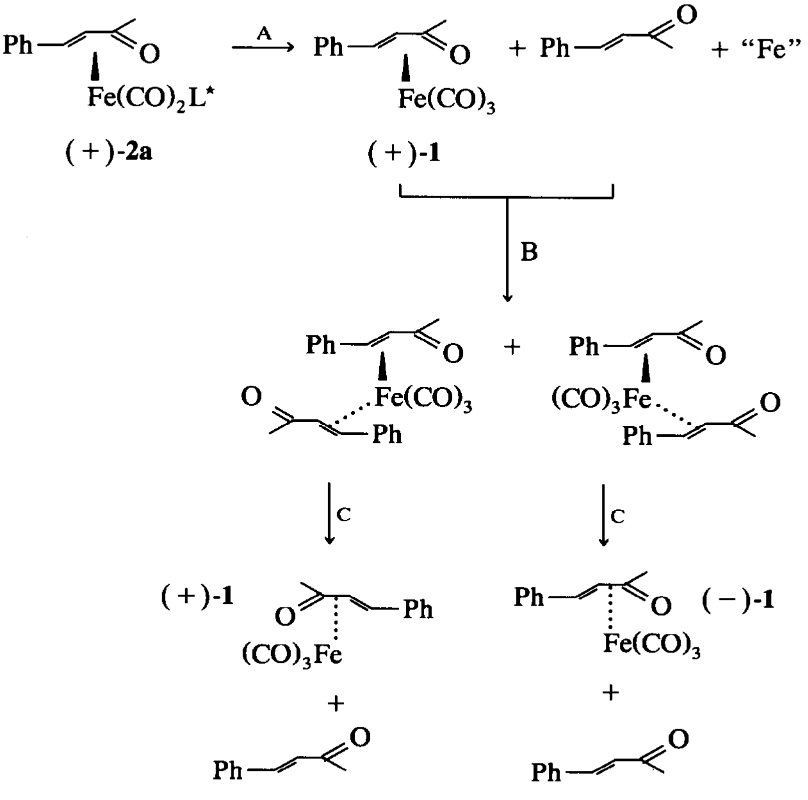
belongs to the C(4) proton of (+)-**1**. The smaller peak up-field is from the C(4) proton of the other enantiomer (−)-**1** (Fig. 4).

Racemizations of (diene)Fe(CO)$_3$-complexes have been described previously [16,17]. Whitlock *et al.* postulated the formation of an intermediate η^2-bonded Fe(CO)$_3$ moiety which can migrate upon heating above 100°C [16]. The complexes we are working with are known transfer reagents, since they are a convenient source of the Fe(CO)$_2$L group (L = CO, phosphines and phosphites) [12,18]. In order to throw light on the reason for the racemization, we tried various reaction conditions:

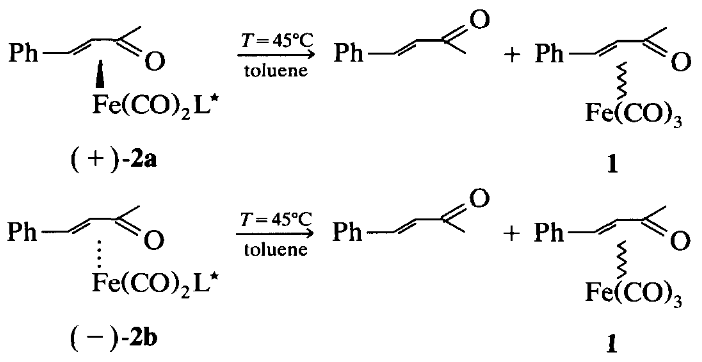
(i) Heating of each diastereomer ((+)-**2a** or (−)-**2b**) in toluene at 45°C in the absence of CO caused no diastereomerization. Some decomposition occurred, giving the free ligand and small amounts of the tricarbonyl complex; this is discussed below. Likewise, heating of diastereomer (+)-**2a** or (−)-**2b** with a 3-fold excess of free benzylideneacetone in toluene at 45°C caused no diastereomerization.

(ii) Heating of enriched (+)-**1** ((+)-**1**/(−)-**1** = 13/1) with free cinnamaldehyde in toluene at 45°C caused a partial transfer of the Fe(CO)$_3$ moiety to the new ligand. The resulting optically active complex [(cinnamaldehyde)Fe(CO)$_3$] has a lower enantiomeric purity ((+)-**4**/(−)-**4** = 5/4) than the starting material, as shown by a chiral shift reagent experiment with Eu(tfc)$_3$.

In the light of these observations we suggest the following pathway for the racemization that occurs during the L*/CO exchange. (The mechanism is shown



Scheme 2. Proposed mechanism for partial racemization of (+)-**1**.



Scheme 3.

for only one of the two possible diastereomers) (Scheme 2). In a first step (step A) the pure diastereomers ((+)-**2a** and (−)-**2b**) undergo ligand displacement at the iron, with retention of the planar chirality to give the enantiomerically pure complexes (+)-**1** and (−)-**1**. Simultaneously, partial decomposition of the starting material releases free benzylideneacetone ligand. Bonded benzylideneacetone can now be displaced by the free ligand via dechelation of the carbonyl group and partial coordination of the new benzylideneacetone ligand (step B). These intermediates then decompose (step C) to give the desired complexes, but with lower optical purity since this transfer reaction can take place at both enantiotopic faces of the new ligand [9]. The best results in terms of enantiomeric purity were obtained by carrying out the reaction at room temperature for 31 h. After heating of (+)-**2a** or (−)-**2b** in toluene (Scheme 3) some decomposition product and a small amount of the Fe(CO)$_3$ complex can be isolated. The latter complex also is of low enantiomeric purity. The mechanism seems to be the same as that described above. The CO is supplied by partial decomposition of starting material. Similar observations were made by Howell with [(η^4-benzylideneacetone)Fe(CO)$_2$L] (L = PPh) [15].

Experimental

The IR spectra were recorded on a Perkin–Elmer 298 spectrometer. CD spectra were recorded on a Jasco J-500A spectrometer. Proton NMR spectra were recorded on a Bruker AC-300 spectrometer at 300 MHz, and ^{13}C and ^{31}P NMR spectra on a Varian XL-200 spectrometer at 50 and 80.7 MHz, respectively. Chemical shifts of ^{31}P spectra are reported relative to H_3PO_4 as external reference. Common solvents were distilled prior to use. All reactions were carried out under nitrogen. Crystallographic data were collected on a Nicolet-R3 diffractometer. The positions of the Fe, P, and three C atoms were located by direct methods. The remaining non-hydrogen atoms were located from subsequent difference Fourier syntheses. Empirical absorption corrections were applied. All of the hydrogen atoms, except H(3) and H(8), could be located in a difference Fourier map, and their positions were refined. Atoms H(3) and H(8) were placed in geometrically calculated positions with a C–H distance of 0.95 Å, and their positions were kept fixed. The non-hydrogen atoms were refined with anisotropic thermal parameters, and the hydrogen atoms with individual isotropic temperature factors. The final difference Fourier maps were featureless except for three peaks of 0.29–0.51 e $Å^{-3}$ near the Fe and P atoms. The structure solution was performed using the direct method routine of SHELXS86 [19], and refinement was performed with the TEXSAN program package [20]. Empirical absorption corrections were applied using DIFABS [21]. A table of H atom coordinates, a full list of bond lengths and angles, and a list of thermal parameters and structure factors are available from the authors.

Preparation of [(+)-(pS)-(benzylideneacetone)Fe(CO)$_2$L] and [(−)-(pR)-(benzylideneacetone)Fe(CO)$_2$L*]*

To a solution of [(η^4-benzylideneacetone)Fe(CO)$_3$] ((rac)-**1**) (0.44 g, 1.54 mmol) and (+)-NMDPP (L*, 0.5 g, 1.54 mmol) in 30 ml of acetonitrile at room temperature was added trimethylamine oxide (0.26 g, 2.33 mmol). On completion of the reaction (15 min) the solvent was removed under reduced pressure. Filtration through Celite and chromatography on silica gel (Merck, 0.040–0.063) with 6/1 hexane/ether as eluent separated the two diastereomers. 0.31 g (0.53 mmol, 35%) of [(*pS*)-(η^4-benzylideneacetone)Fe(CO)$_2$L*] ((+)-**2a**) and 0.27 g (0.46 mmol, 30%) of [(*pR*)-(η^4-benzylideneacetone)Fe(CO)$_2$L*] ((−)**2b**) were isolated as yellow crystals.

[(+)-(pS)-(η^4-Benzylideneacetone)Fe(CO)$_2$L] ((+)-2a).* $[\alpha]_D$ (20°) = +1166 ± 50 (CH_2Cl_2, $c = 0.155$). $R_f = 0.31$ (hexane/ether = 6/1). IR (CH_2Cl_2): 3000–2800, 1995, 1933 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.8–7.0 (m, 15H, phenyl-H), 5.63–5.32 (m, 1H, H-C(3)), 3.1 (m, 1H, H-C(13)), 2.41 (d, *J*(PH) 2.3 Hz, 3H, H-C(1)), 2.04–1.26 (m, 10H, H-C(4), CH_2 and CH protons), 1.17 (d, *J*(HH) 7.2 Hz, CH_3), 0.62 (d, *J*(HH) 6.7 Hz, CH_3), 0.31 (d, *J*(HH) 6.1 Hz, CH_3). ^{31}P NMR (acetone-d_6): 59.4 (s). ^{13}C NMR (CD_2Cl_2): 215.3 (s, CO), 210.5 (s, CO), 143.0 (s, C(2)), 139.8–125.5 (18C, phenyl-C), 80.7 (s, C(3)), 61.3 (s, C(4)), 40.0 (s, CH), 36.9 (d, *J*(PC) 16 Hz, CH), 31.2 (s, CH), 31.1 (s, CH_2), 28.9 (s, CH_2), 28.7 (s, CH), 23.9 (s, CH_3), 21.6 (s, CH_3), 20.8 (d, *J*(PC) 11 Hz, CH_2), 20.6 (s, CH_3), 18.2 (s, CH_3).

[(−)-(pR)-(η^4-Benzylideneacetone)Fe(CO)$_2$L] ((−)-2b).* $[\alpha]_D$ (20°) = −1066 ± 50 (CH_2Cl_2, $c = 0.155$). $R_f = 0.18$ (hexane/ether = 6/1). IR (CH_2Cl_2): 3000–2800, 1995, 1933 cm^{-1}. ^1H NMR (CD_2Cl_2): 7.6–6.7 (m, 15H, phenyl-H), 5.61 (dd, *J* 8.7, 2.0 Hz, 1H, H-C(3)), 3.27 (m, 1H, H-C(13)), 2.46 (d, *J*(PH) 2.3 Hz, 3H, H-C(1)), 2.42–1.22 (m, 10H, H-C(4), CH_2 and CH protons), 1.14 (d, *J*(HH) 6.9, CH_3), 0.72 (d, *J*(HH) 6.6 Hz, CH_3), 0.31 (d, *J*(HH) 6.1 Hz, CH_3). ^{31}P NMR (acetone-d_6): 58.1 (s). ^{13}C NMR (CD_2Cl_2): 215.2 (d, *J*(PC) 11 Hz, CO), 210.3 (s, CO), 142.3 (s, C(2)), 135.8–125.2 (18C, phenyl-C), 79.9 (s, C(3)), 61.7 (s, C(4)), 40.3 (s, CH), 39.2 (d, *J*(PC) 18 Hz, CH), 31.3 (s, CH_2), 30.8 (s, CH), 29.0 (s, CH_2), 28.5 (d, *J*(PC) 8 Hz, CH), 24.2 (s, CH_3), 21.7 (s, CH_3), 21.4 (d, *J*(PC) 11 Hz, CH_2), 20.5 (s, CH_3), 18.0 (s, CH_3).

Synthesis of optically active [(η^4-benzylidene-acetone)Fe(CO)$_3$]

A solution of diastereomerically-pure [(η^4-benzylideneacetone)Fe(CO)$_2$L*] complex ((+)-**2a** or (−)-**2b**)) (0.33 g, 0.57 mmol) in toluene (20 ml) was flushed with CO for 5 min and a balloon filled with CO was placed on the top of the reaction flask. The reaction was carried out at various temperatures, *viz.* 25, 45 and 65°C. After evaporation of the solvent at room temperature under high vacuum, chromatography on silica gel with 6/1 hexane/ether as eluent gave the optically active $Fe(CO)_3$ complexes as red crystals. Yields are dependent on the reaction temperature (*T* 65°C/*t* 2.5 h, yield 89%; *T* 45°C/*t* 2.5 h, yield 67%; *T* 25°C/*t* 31 h, yield 50%). At higher temperatures more decomposition product was formed. The optical purities of the products obtained in these displacement reactions are listed in Table 4. The identity of [(η^4-benzylideneacetone)$Fe(CO)_3$] was confirmed by comparison of its ^1H NMR spectrum with that in the literature [12]. The specific rotation of pure (+)-**1** was extrapolated to $[\alpha]_D$ (20°) = +936 ± 30 (CH_2Cl_2, $c = 0.155$).

Synthesis of optically active [η^4-(cinnamaldehyde)$Fe(CO)_3$]

The starting complex (enriched [(benzylideneacetone)$Fe(CO)_3$], (+)-**1**/(−)-**1** = 13/1, 0.1 g, 0.35 mmol) was treated with a 3-fold excess of cinnamaldehyde at 45°C in toluene (10 ml). After 2.5 h the solvent was evaporated at room temperature under high vacuum and the crude product chromatographed on silica gel with 6/1 hexane/ether as eluent to give 83 mg (87%) of [(η^4-cinnamaldehyde)$Fe(CO)_3$] as a dark red oil. The product has a lower enantiomeric purity than the starting material ((+)-**4**/(−)-**4** = 5/4). For physical data see ref. 22.

Acknowledgement

This work was supported by the Swiss National Science Foundation.

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