Preliminary communication

Diastereoisomer separation and absolute configuration of (methylsorbate)Fe(CO)$_2$L, (sorbaldehyde)Fe(CO)$_2$L and (1-methoxycyclohexadiene)Fe(CO)$_2$L (L = (+)-neomenthyl(PPh$_2$))

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Abstract

Substitution of CO in (methylsorbate)-, (sorbaldehyde)- and (1-methoxycyclohe-xadiene)-Fe(CO)$_2$L by (+)-(neomenthyl)PPh$_2$ allows facile diastereoisomer separation. The absolute configurations have been established by X-ray crystallography and circular dichroism spectroscopy.

The application of (diene)Fe(CO)$_3$ and [(dienyl)Fe(CO)$_3$]X compounds in enantioselective synthesis [1] depends on the availability of a range of fully resolved complexes of known absolute configuration. Most reported resolution methods are diene- or dienyl-based, and rely on either addition of chiral nucleophiles to cyclic dienyl systems [2], or classical resolution of complexes containing suitable functional groups (CHO, COOH) [3]. We recently outlined the potential of chiral phosphines in this respect using fractional crystallization of diastereoisomeric (diene)Fe(CO)$_2$L* pairs (L* = chiral phosphine) [4]. In many cases, successful diastereoisomer separation may also be achieved chromatographically, and below we report application of this method to two classes of complex of some current utility in organic synthesis, together with assignments of absolute configuration.

Phosphine substitution [5] of **1** and **2** using (+)-(neomenthyl)PPh$_2$ yields equimolar diastereoisomeric mixtures **3a**, **3b** and **4a**, **4b** that can be quantitatively
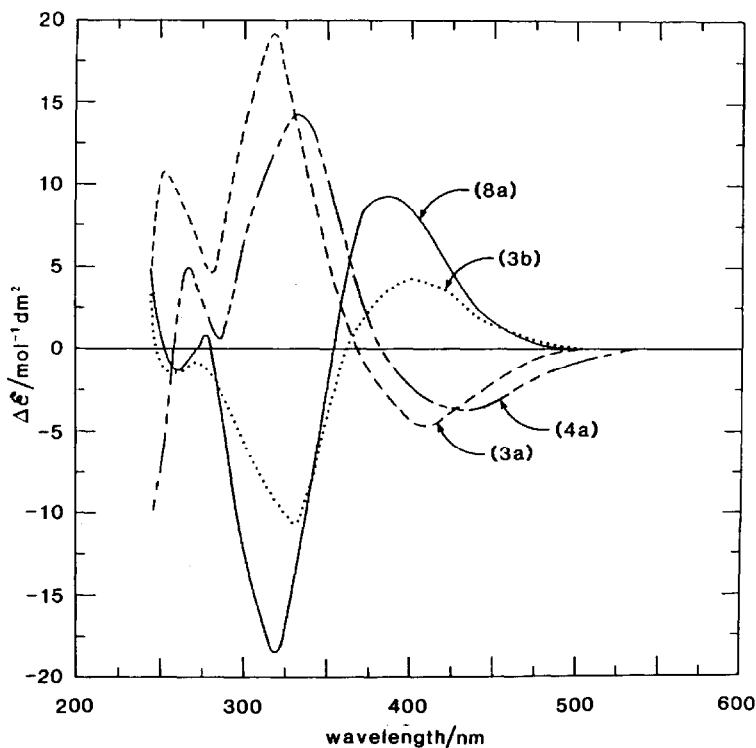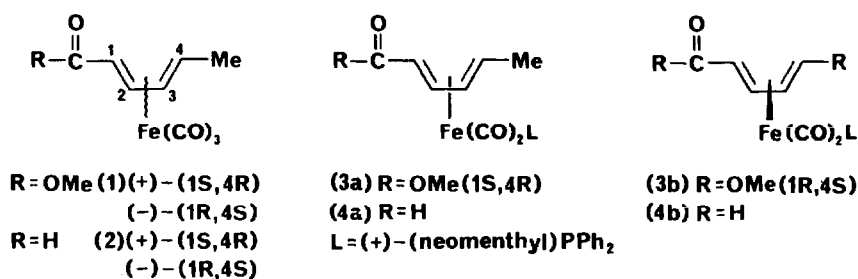
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Fig. 1. Circular dichroism spectra.

separated by preparative TLC [6*]. The almost mirror image nature of the circular dichroism spectra of **3a**, **3b** (Fig. 1) in the 250–550 nm region indicates little perturbation of these bands by the chiral phosphine, which is itself transparent in this region. Thus, the spectrum of **4a** is essentially superposable on that of **3a**, and the relationship to the tricarbonyl has been established by conversion of (−)-**1**, 12% enriched and obtained by asymmetric complexation [7] into a diastereoisomeric mixture of **3a**, **3b** which is 12% enriched in **3b**.

R = OMe (1)(+)−(1S,4R)
        (−)−(1R,4S)
R = H   (2)(+)−(1S,4R)
        (−)−(1R,4S)

(3a) R = OMe(1S,4R)
(4a) R = H
L = (+)−(neomenthyl)PPh₂

(3b) R = OMe(1R,4S)
(4b) R = H

The absolute planar configurations shown have been established from a crystallographic analysis [6*] of **3a** (Fig. 2). The unit cell contains two crystallographically independent molecules of essentially identical dimensions, and the overall molecular geometry (Fig. 2) is that of a distorted square pyramid with phosphine in the axial position. The known configuration of the neomenthyl group (1S, 2S, 5R) establishes the configuration of the (methylsorbate)Fe moiety as (1S, 4R).

In a similar way [6*], complexes **5a**, **5b** may be quantitatively separated and the absolute planar configurations established by conversion of **5a** to an 85/15 mixture

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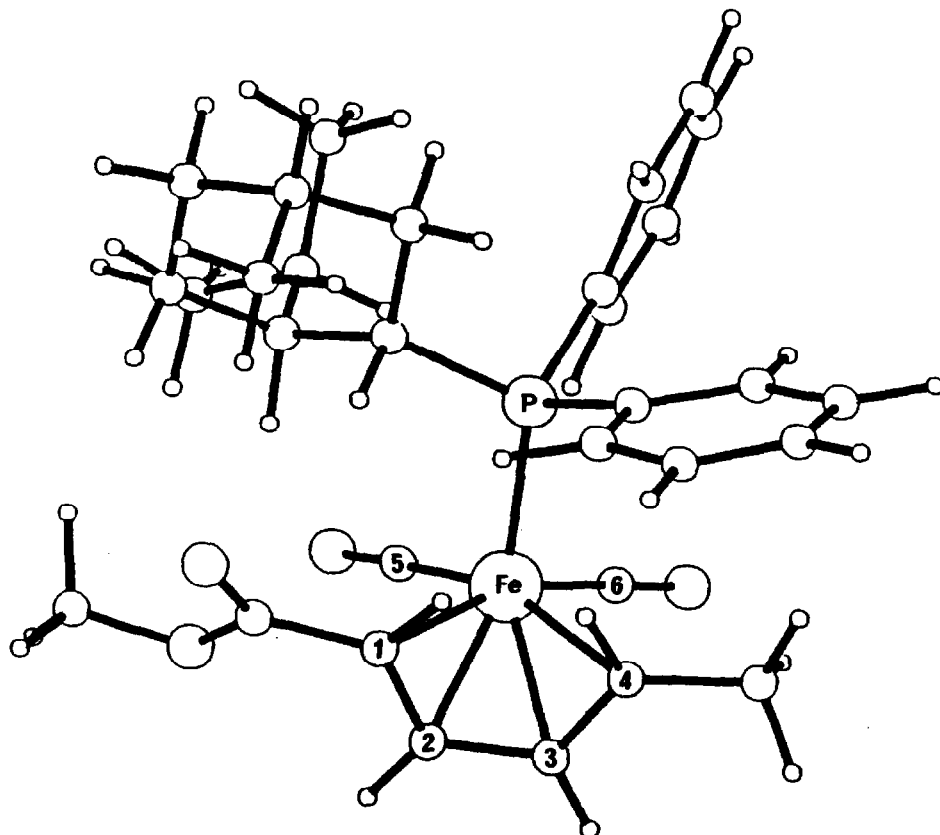* Reference number with asterisk indicates a note in the list of references.

Fig. 2. Structure of complex **3a**. Important bond lengths (Å): Fe–P, 2.265(4); Fe–C(1), C(4) 2.180(3), 2.166(12); Fe–C(2), C(3) 2.031(14), 2.058(13); Fe–C(5)O, C(6)O 1.711(18), 1.723(15); C(1)–C(2), C(3)–C(4) 1.437(16), 1.402(16); C(2)–C(3) 1.361(18). Important bond angles (°): P–Fe–C(15), C(6) 101.9(5), 99.9(4); P–Fe–C(4) C(4) 96.5(3), 98.8(4); C(1)–Fe–C(4) 77.6(5); C(2)–Fe–C(3) 38.9(5); C(5)–Fe–C(6) 88.4(7).

of **6a/7a** followed by hydrolysis of **6a** to give **8a**. Comparison of the CD spectrum of **8a** (Fig. 1) with that of (+)-(cyclohexadienone)Fe(CO)₃ of known (2R) configuration [11] establishes the absolute configurations of the diastereoisomer pairs shown, and it is known that (−)-(1-methoxycyclohexadiene)Fe(CO)₃ possesses the (1R) configuration [12]. We are currently examining the diastereoisomeric sep-

(R configurations shown)

i. Ph₃CPF₆, CH₂Cl₂, RT

ii. aqueous acetone, 40°C
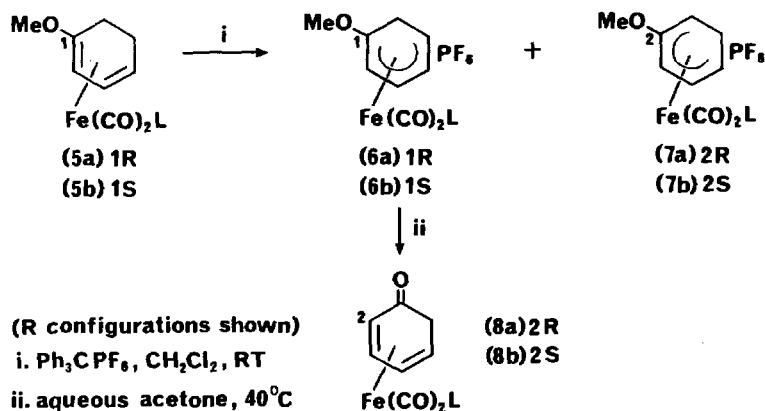
aration of (1-alkoxy-4-alkylcyclohexadiene)Fe(CO)$_3$ complexes which, in contrast to **5a/5b** undergo regioselective formation of [(2-alkoxy-5-alkylcyclohexadienyl)Fe (CO)$_3$]X salts of utility in natural product synthesis [13].

References

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6 Preparative TLC of **3a**, **3b** on silica (95/5 petroleum ether/ethyl acetate) gave **3a** ($\delta(^{31}$P) 66.9 ppm, broad) and **3b** (67.9 ppm) in order of elution. Complexes **4a** and **4b** were obtained similarly using 90/10 petroleum ether/ethyl acetate; only a single broadened ^{31}P resonance is observed at $+20\,^{\circ}$C, but individual resonances may be easily distinguished at $-50\,^{\circ}$C (**4a**: 65.0 ppm; **4b**: 65.8 ppm). The fluxional behaviour will be discussed in a full paper. Complexes **5a**, **5b** were separated using 98/2 petroleum ether/ethylacetate to give **5a** (72.7 ppm) and **5b** (68.9 ppm) in order of elution. Satisfactory analytical and spectroscopic data were obtained for all complexes.

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8 Crystal data; C$_{31}$H$_{39}$O$_4$PFe, orthorhombic, space group $P2_12_12_1$, a 9.860(2), b 35.815(4), c 16.519(1) Å, $Z = 8$, U 5833.50 Å^3. The structure was solved by a combination of Patterson search and direct methods (SHELX86) [9] and refined by full matrix least squares (SHELX76) [10] with 2080 reflections which had $I > 3\sigma(I)$ and 307 variables. Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atoms were included in calculated positions; only the iron atoms 2 were refined anisotropically. In the final least squares cycle, the largest shift/ESD in any parameter was 0.001 and in the difference map the maximum and minimum excursions were 0.175 and -0.13 e/Å^3. The residuals were $R = 0.0376$ and $R_w = 0.0388$.

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