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Synthetic and kinetic studies of the reaction of amino acid esters with tricarbonyl(dienyl)iron cations

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Abstract

Amino acid esters add rapidly and reversibly to the dienyl iron cations $[Fe(CO)_3(2\text{-}XC_6H_6)]^+$ (**Ia**, X = MeO; **Ib**, X = H) to give first the cation adducts **II** and then the neutral adducts **III**, as follows: $[Fe(CO)_3(XC_6H_6)]^+$ (**I**) + $H_2NCH(R)CO_2Et \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CO)_3\{XC_6H_6 \cdot NH_2CH(R)CO_2Et\}]^+$ (**II**) $\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(CO)_3\{XC_6H_6 \cdot NHCH(R)(CO_2Et)\}]$ (**III**).

Results of ^1H NMR spectral studies confirm that the addition of the amino acid esters to the dienyl rings of (**I**) is exo. With the chiral substrate **Ia**, moderate chiral discrimination occurs in the attack of (*R*)-amino acid esters, providing a new route to optically active **Ia**. Kinetic studies of the reactions reveal the general rate law, Rate = k[Fe][RNH_2]; this observation may be rationalized in terms of a mechanism involving the steady-state formation of the intermediate **II**. Since $k_2[RNH_2]$ can be expected to be $\gg k_{-1}$ (and k_{-2} negligible), the second-order rate constants k equate with k_1 for the initial ring addition step. The large negative entropies of activation support such a bimolecular process. The data permit amino acid esters to be placed in a quantitative order of nucleophility with some 40 other nucleophiles towards cation **Ib**.

Key words: Iron; Carbonyl; Amino acid; Kinetics

Introduction

There has been considerable recent interest in the synthesis of optically active $[Fe(CO)_3(\pi\text{-hydrocarbon})]^{n+}$ (hydrocarbon = diene or dienyl; $n = 0$ or 1) complexes and their potential use in asymmetric synthesis [1–3]. Methods currently available for the synthesis of partially or fully resolved complexes include classical diastereomer separation [3–5], reaction of 1,3-dienes with chiral transfer agents such as (+)-(pulegone) iron tricarbonyl [6] and diastereostereomeric selection during the reaction of a chiral dienyl cation with optically active nucleophiles [7–9]. We have explored the latter approach extensively with tertiary phosphines nucleophiles, and shown it to provide a convenient and facile route to optically active $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-dienyl})]^+$ complexes [8,10].

Although biological systems provide an extensive array of potential nucleophiles, their interaction with electrophilic organometallic species has to date been virtually unexplored. As part of a programme of investigation of such interactions and their utility, we report here studies of the extent and mechanism of chiral discrimination in the reaction of amino acid esters with the chiral iron dienyl substrate $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-MeO} \cdot C_6H_6)]BF_4$ (**Ia**).

These reactions proceed via the two-step sequence shown in Scheme 1 (X = H, MeO). Both cationic (**II**) and neutral (**III**) adducts have been isolated and characterized by ^1H NMR and IR spectroscopy and fast atom bombardment (FAB) mass spectrometry. By varying the nature of the amino acid substituent R (Me, $CH(Me)_2$, CH_2Ph, Ph), the influence of steric factors in controlling diastereotopic discrimination has been

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determined. Kinetic studies of reactions (1) and the related reactions with the achiral parent dienyl complex $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)]^+$ (**Ib**) are also reported, allowing amino acid esters to be placed in a quantitative nucleophilicity order.

2. Experimental details

2.1. Materials

The complex salts $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}C_6H_7)][BF]_4$ (**Ib**) and racemic $(2R,2S)$-$[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)][BF]_4$ (**Ia**) were prepared and purified by published procedures [11].

The amino acid ester nucleophiles were purchased from Aldrich as 99% resolved hydrochloride salts. The neutral amino acid esters were liberated by the following procedure: the appropriate salt (*ca.* 0.5 g) was suspended in chloroform (*ca.* 30 cm^3) and ammonia bubbled through with stirring for 10 min. The resulting white precipitate of ammonium chloride was filtered off, and the filtrate rotary-evaporated to dryness *in vacuo* at 30°C to give the product as a clear oil. The amino acid esters were stored in a freezer under dinitrogen. Their purity was checked before use by ^1H NMR spectroscopy; *e.g.* the absence of alcohol signals confirmed that no cyclization had occurred.

Diethyl ether (A.R. grade) was dried over sodium wire before use. Acetonitrile solvent (BDH) was distilled in bulk and stored over molecular sieves (A4) under dinitrogen. All over solvents were of SLR grade.

2.2. Synthesis of cationic tricarbonyl (1-4-η-5-N-amino acid ester-cyclohexa-1,3-diene) iron tetrafluoroborate adducts (II)

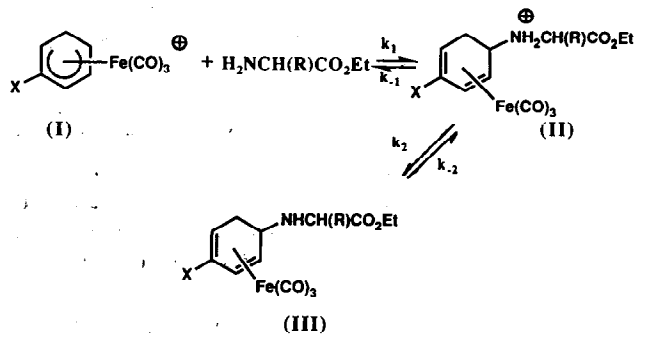
2.2.1. Method A

2.2.1.1. Tricarbonyl (1-4-η-5-N-glycine ethyl ester-cyclohexa-1,3-diene) iron tetrafluoroborate The dienyl salt (**Ib**) (0.15 g, 0.5 mmol) was mixed with freshly prepared glycine ethyl ester (0.16 g, 1.5 mmol) in acetonitrile (15 cm^3). The mixture was stirred under dinitrogen at room temperature for 30 min, and the volume then reduced to *ca.* 2 cm^3. This solution was passed through a short silica (230–400 mesh) column, with acetonitrile as eluant. The yellow band was collected, and rotary evaporation gave a yellow oily solid (0.13 g, 83%). ν(CO) (CH_3CN) 2052, 1980 cm^{-1}. Anal. Found: C, 38.2; H, 3.3; N, 2.8. $C_{13}H_{15}O_5NBF_4Fe$ calc: C, 38.3; H, 3.7; N, 3.4%.

^1H NMR (400 MHz, CD_3COCD_3): σ 5.87 (1H, t, H^2, $J_{2,3} \sim J_{2,1} \sim 5$ Hz); 5.82 (1H, t, H^3, $J_{2,3} \sim J_{3,4} \sim 4.7$ Hz); 4.25 (2H, q, OCH_2CH_3, $J(CH_2, CH_3) = 7.2$ Hz); 4.05 (3H, overlapping peaks, H_2NCH_2CO– and $H^{5'}$); 3.27 (1H, m, H^1); 3.24 (1H, m, H^4); 2.51 (1H, septuplet, $H^{6'}$, $J_{6',6} = 16.0$ Hz, $J_{6',5'} = 10.9$ Hz, $J_{6',1} = 3.8$ Hz); 1.98 (1H, d, H^6, $J_{6,6'} = 15.4$ Hz); 1.25 ppm (3H, t, OCH_2CH_3, $J(CH_2, CH_3) = 7.2$ Hz). FAB mass spectrum: m/z 410 $(M + 1)^+$, 219 $(M - glyOEt)^+$, 191 $(M - glyOEt - CO)^+$, 163 $(M - glyOEt - 2CO)^+$, 135 $(M - glyOEt - 3CO)$, 104 $(glyOEt + 1)^+$.

2.2.1.2. Tricarbonyl (1-4-η-5-N-alanine ethyl ester-cyclohexa-1,3-diene) iron tetrafluoroborate An analogous reaction between the dienyl salt **Ib** and alanine ethyl ester gave the cationic adduct **IIb** in 93% yield as an oily yellow solid. ν(CO)(CH_3CN): 2052, 1980 cm^{-1} Anal. Found: C, 39.5; H, 4.6. $C_{14}H_{17}O_5NBF_4Fe$ calc.: C, 39.7; H, 4.5%.

^1H NMR (400 MHz, $CDCl_3$); σ 5.82 (1H, m, H^2); 5.74 (1H, m, H^3); 4.26 (2H, m, diast. OCH_2CH_3); 4.14, 4.10 (1H, overlapping quartets, diast. $-H_2NCH(Me)CO-$, J(CH, Me) = 7.0 Hz); 3.9 (1H, overlapping double triplets, diast. $H^{5'}$, $J_{5',6'}$ 10.2, 10.4 Hz, $J_{5',4} \sim J_{5',6} \sim 4$ Hz); 3.25 (1H, m, H^1); 3.20 (1H, m, H^4); 2.43 (1H, m, $H^{6'}$); 1.85, 1.81 (1H, overlapping doublets, diast. H^6, $J_{6,6'} = 16.2$ Hz); 1.53, 1.51 (3H, overlapping doublets, $-NH_2CH(CH_3)-$, J(CH, CH_3) = 7.2, 7.3 Hz); 1.28 ppm (3H, m, $-OCH_2CH_3$). FAB mass spectrum: m/z 424 $(M + 1)^+$, 323, 235, 219 $(M - ala\ OEt)^+$, 191 $(M - alaOEt - CO)^+$, 163 $(M - alaOEt - 2CO)^+$, 135 $(M - alaOEt - 3CO)^+$, 118 $(alaOEt + 1)^+$.



Scheme 1.

2.2.2. Method B

A variation on the above route involving use of equimolar amounts of the dienyl salt and amino acid ester, followed by the addition of diethyl ether to the reaction solution, generally led to mixtures, as illustrated below for the reaction between dienyl salt **Ia** and alanine ethyl ester.

To a solution of salt **Ia** (0.134 g, 0.40 mmol) in CH_3CN (2 cm^3) was added a solution of alanine ethyl ester (0.046 g, 0.40 mmol) in CH_3CN (2 cm^3) under dinitrogen. Addition of excess diethyl ether gave a pale

TABLE 1. IR spectra of cationic and neutral adducts from the reaction of $[Fe(CO)_3$ (1-5-η-2-$MeOC_6H_6)]BF_4$ with amino acid esters in CH_3CN

Amino acid	ν(CO) (cm^{-1})	
	Cationic adduct	Neutral adduct
Alanine	2066, 1988	2056, 1981
Valine	2067, 1989	2052, 1981
Phenylalanine	2068, 1990	2050, 1982
Phenylglycine	2066, 1990	2052, 1980

cream precipitate of unchanged **Ia** (0.043 g, 32%), which was filtered off at the pump. ν(CO)(CH_3CN): 2115, 2060 cm^{-1}.

Rotary evaporation of the filtrate gave a yellow oil, which from its IR spectrum was an *ca.* 90/10 mixture of the desired cationic adduct $[Fe(CO)_3(EtO_2CCH(Me)NH_2 \cdot C_6H_6\text{–}OMe)]^+$ (**IIb**) (ν(CO) (acetone): 2055, 1980 cm^{-1}; $\nu(CO_2Et)$ (Nujol): 1740 cm^{-1}) and starting dienyl complex **Ia**.

In an attempt at further purification, this latter mixture was dissolved in acetone (1 cm^3) and an excess of diethyl ether added. This yielded a further precipitate of starting complex **Ia**, and rotary evaporation of the filtrate gave an *ca.* 50/50 mixture of the cationic adduct **IIb** and the neutral adduct $[Fe(CO)_3(EtO_2CCH(Me)NH \cdot C_6H_6OMe)]$ (**IIIb**). ν(CO)(CH_3CN): 2044, 1970 cm^{-1}.

2.2.3. In situ synthesis of related cationic adducts

Each of the other cationic adducts **II** were prepared *in situ* by mixing the dienyl salt **Ia** with the appropriate amino acid ester in a 1:1 ratio. They were identified by their characteristic IR ν(CO) bands at *ca.* 2050 and 1980 cm^{-1}, and from their ^1H NMR spectra (Table 1).

2.3. Synthesis of neutral tricarbonyl (1-4-η-5-N-amino acid ester-cyclohexa-1,3-diene) iron adducts (III)

The corresponding neutral adducts **III** could be prepared in general by treatment of the above cationic adducts with either excess amine or ammonia gas.

2.3.1. Tricarbonyl (1-4-η-2-methoxy-5-N-valine ethyl ester-cyclohexa-1,3-diene) iron (IIIa)

Valine ethyl ester (0.039 g, 0.27 mmol) and solid dienyl salt **Ia** (0.086 g, 0.26 mmol) were weighed into a reaction vessel under dinitrogen and dissolved in acetonitrile (5 cm^3). After 15 min reaction, to give the cationic adduct, ammonia gas was bubbled through for 10 min. Rotary evaporation yielded a yellow oil, which was extracted with diethyl ether (3×5 cm^3). Filtration and further rotary evaporation gave the neutral adduct **IIIa** as a pale yellow oil (0.077 g, 84%). ν(CO)(CH_3CN): 2044, 1971 cm^{-1}. Anal. Found: C, 51.9; H, 6.2; N, 4.2. $C_{17}H_{23}O_6FeN$ calc.: C, 51.9; H, 5.9; N, 3.6%.

2.3.2. Tricarbonyl (1-4-η-5-N-glycine ethylester-cyclohexa-1,3-diene) iron (IIIb)

An analogous reaction between the dienyl salt **Ib** and glycine ethyl ester gave the neutral adduct **IIIb** in 70% yield as a yellow oil. Anal. Found: C, 48.4; H, 4.5. $C_{13}H_{14}O_5NFe$ calc.: C, 48.6; H, 4.7%.

^1H NMR (400 MHz, CD_3COCD_3): σ 5.68 (1H, t, H^2, $J_{2,3} \sim J_{2,1} \sim 5.2$ Hz); 5.56 (1H, t, H^3, $J_{3,2} \sim J_{3,4} \sim 5.0$ Hz); 4.12 (2H, q, OCH_2CH_3, $J(CH_2, CH_3) = 7.1$ Hz); 3.3 (3H, overlapping peaks, $HNCH_2CO$ and $H^{5'}$); 3.19 (1H, m, H^1); 3.06 (1H, m, H^4); 2.15 (1H, septuplet, $H^{6'}$, $J_{6',6} = 15.2$ Hz, $J_{6',5'} = 10.3$ Hz, $J_{6',1} = 4.2$ Hz); 1.38 (1H, d, H^6, $J_{6,6'} = 15.1$ Hz); 1.22 ppm (3H, t, OCH_2, CH_3, $J(CH_2, CH_3) = 7.1$ Hz). ν(CO)(CH_3CN): 2042, 1970 cm^{-1}.

2.3.3. Tricarbonyl (1-4-η-5-N-alanine ethylester-cyclohexa-1,3-diene) iron (IIIc)

An analogous reaction between the dienyl salt **Ib** and alanine ethyl ester gave the neutral adduct **IIIc** in 92% yield as a yellow oil. Anal. Found: C, 50.2; H, 5.1. $C_{14}H_{16}O_5NFe$ calc.: C, 50.1; H, 5.1%.

^1H NMR (400 MHz, $CDCl_3$): σ 5.72 (1H, m, H^2); 5.58 (1H, m, H^3); 4.12, (2H, m, diast. OCH_2CH_3); 3.44, 3.35 (1H, quartets, diast. –$NHCH$(Me)CO–, $J(CH, CH_3) = 7.1$ Hz); 3.2 (1H, m, $H^{5'}$); 3.13 (1H, m, H^1); 3.00 (1H, m, H^4); 2.26 (1H, m, $H^{6'}$); 1.45, 1.38 (1H, doublets, diast. H^6, $J_{6',6} = 15.1$, 16.8 Hz); 1.25 (3H, m, $-NHCH(CH_3)-$); *ca.* 1.15 (3H, m, $-OCH_2CH_3$). ν(CO)(CH_3CN): 2040, 1970 cm^{-1}.

2.3.4. In situ synthesis of related neutral adducts

Each of these adducts and the other neutral adducts were also prepared quantitatively *in situ* by adding a ≥ 4 molar excess of the appropriate amino acid ester to the dienyl salt **Ia** or **Ib** (see IR equilibrium experiments below), or by adding di-isopropylethylamine to the cationic adduct. For example, addition of a drop of di-isopropylethylamine to a CD_3CN or CD_3COCD_3 solution of the cationic adduct $[Fe(CO)_3(EtOOCCH(R)NH_2 \cdot C_6H_7)]BF_4$ (R = H, MeO) caused immediate deprotonation and the quantitative *in situ* formation of the neutral adduct $[Fe(CO)_3(EtOOCCH(R)NH \cdot C_6H_7)]$ (**III**).

2.4. Synthesis of optically active tricarbonyl (1-5-η-2-methoxycyclohexadienyl) iron tetrafluoroborate

$[Fe(CO)_3(2\text{-}MeOC_6H_6)]BF_4$ (**Ia**) was prepared in optically active form by making use of chiral discrimination in the reaction of racemic (2*R*, 2*S*) **Ia** with the optically active amino acid esters. In general, racemic **Ia** was treated with the appropriate amino acid ester in the molar ratio dienyl/nucleophile of 1:0.5. Un-

changed dienyl salt was recovered from solution by addition of diethyl ether, and its optical purity calculated by comparison of its CD spectrum with that reported for the fully resolved complex.

2.4.1. Reaction of racemic Ia with (S)-alanine ethyl ester

In acetone. A solution of (*S*)-alanine ethyl ester (0.059 g, 0.504 m mol) in acetone (2 cm^3) was added

TABLE 2. ^1H NMR data for diastereomeric cationic $[Fe(CO)_3(1\text{-}4\text{-}\eta\text{-}5\text{-}N\text{-}RNH_2 \cdot C_6H_6OMe)]^+$ adducts in CD_3CN

Adduct	Proton	Shift (ppm)	Coupling (Hz)
$RNH_2{=}NH_2{-}C(CH_3)(H){-}CO_2CH_2CH_3$	1	3.28	$J_{1,6} = 3.2$, $J_{1,6'} = 3.1$
	3	5.43 [a], 5.40	$J_{3,4} = 6.5$
	4	3.7 [b]	
	5′	*ca.* 3.7 [b]	
	6	1.84 [a], 1.80	$J_{5',6} = 3.2, 3.1$
	6′	2.36 [a], 2.41	
	-O*Me*	3.73	
	-C*H*	3.96 [a], 4.00	J(CH,Me) = 7.3, 7.2
	-C*Me*	1.48 [a], 1.51	
	$-CO_2CH_2$	4.29 [a], 4.28	$J(CH_2, CH_3) = 7.1, 7.1$
	$-CH_2CH_3$	1.31 [a], 1.30	
$RNH_2{=}NH_2{-}C(CH_2Ph)(H){-}CO_2CH_3$	1	3.24	
	3	5.33 [a], 5.27	$J_{3,4} = 6.8, 6.0$
	4	3.56	$J_{4,5'} = 5.1$
	5′	*ca.* 3.7 [b]	
	6	1.75 [a], 1.71	$J_{6,6'} = 14.7$
	6′	2.30 [a], 2.27	
	-OMe	3.70	
	-C*H*	4.02	
	$-CH_2Ph$	3.10	
	-Ph	7.28 [c]	
	$-CO_2Me$	3.71 [a], 3.68	
$RNH_2{=}NH_2{-}C(CHMe_2)(H){-}CO_2CH_2CH_3$	1	3.28	
	3	5.30 [a], 5.36	$J_{3,4} = 3.7, 4.0$
	4	3.62	$J_{4,5'} = 6.0, 6.0$
	5′	*ca.* 3.7 [b]	
	6	1.81, 1.87	
	6′	2.24	$J_{6,6'} = 15.7$
	-O*Me*	3.71	
	-C*H*	3.7 [b]	
	$-CHMe_2$	2.30	$J_{CH,Me} = 7.0$
	$-CHMe_2$	1.03 [a], 0.95	
	$-CO_2CH_2$	4.28 [a], 4.29	$J_{CH_2,CH_3} = 7.3$
	$-CH_2CH_3$	1.30	
$RNH_2{=}NH_2{-}C(Ph)(H){-}CO_2CH_2CH_3$	1	3.25	
	3	5.39 [a], 5.35	$J_{3,4} = 6.1, 6.1$
	4	3.46	
	5′	3.64	
	6	1.87 [a], 1.74	$J_{5',6} = 3.3, 3.3$
	6′	2.22 [a], 2.29	
	-O*Me*	3.71 [a], 3.70	
	-C*H*	4.95 [a], 4.94	
	-Ph	7.42	
	$-CO_2CH_2$	4.27 [a], 4.37	$J_{CH_2,CH_3} = 7.2$
	$-CH_2CH_3$	1.17	

[a] The more abundant diastereomer of the pair. [b] Partly obscured by -OMe signal. [c] Broad band of aromatic signals.

dropwise with stirring to a solution of racemic **Ia** (0.282 g, 0.840 mmol) in acetone (20 cm^3). An excess of diethyl ether was added, giving a cloudy white precipitate of unchanged **Ia**, which was filtered off at the pump and sucked dry (0.140 g, 50%). $\nu(CO) = 2120$, 2068 cm^{-1}. $\Delta\epsilon_{358} = 0.300$ dm^2 mol^{-1}.

In acetonitrile. A solution of (*S*)-alanine ethyl ester (0.0335 g, 0.286 mmol) in acetonitrile (5 cm^3) was added dropwise with stirring to a solution of racemic **Ia** (0.153 g, 0.456 mmol) in acetonitrile (15 cm^3). Addition of an excess of diethyl ether gave 0.053 g of unchanged **Ia** ($\Delta\epsilon_{358} = 0.47$ dm^2 mol^{-1}).

2.4.2. Reaction of racemic Ia with S-valine ethyl ester

A solution of the ester (0.020 g, 0.136 mmol) in acetonitrile (2 cm^3) was added dropwise with stirring to a solution of racemic **Ia** (0.079 g, 0.236 mmol) in acetonitrile (2 cm^3). An excess of diethyl ether was added, giving a cream precipitate of unchanged **Ia**, which was filtered off at the pump and sucked dry (0.038 g, 48%). $\nu(CO) = 2122$, 2068 cm^{-1}. $\Delta\epsilon_{358} = 0.509$ dm^2 mol^{-1}.

2.4.3. Reaction of racemic Ia with S-phenylalanine methyl ester

A solution of the ester (0.041 g, 0.231 mmol) in acetone (5 cm^3) was added dropwise with stirring to a solution of racemic **Ia** (0.154 g, 0.459 mmol) in acetone (10 cm^3). An excess of diethyl ether was added giving a precipitate of unchanged **Ia** which was filtered off at the pump and sucked dry (0.070 g, 45%). $\nu(CO) = 2119$, 2068 cm^{-1}. $\Delta\epsilon_{358} = 0.122$ dm^2 mol^{-1}.

2.4.4. Reaction of racemic Ia with R-phenylglycine ethyl ester

A solution of the ester (0.035 g, 0.197 mmol) in acetonitrile (2 cm^3) was added dropwise with stirring to a solution of racemic **Ia** (0.095 g, 0.284 mmol) in acetonitrile (2 cm^3). An excess of diethyl ether was immediately added, giving a precipitate of unchanged **Ia**, which was filtered off at the pump and sucked dry (0.048 g, 50%). $\nu(CO) = 2120$, 2070 cm^{-1}. $\Delta\epsilon_{358} = -0.606$ dm^2 mol^{-1}. The optical purity of all recovered dienyl salts are summarized in Table 3.

2.5. IR equilibrium studies

Acetonitrile solutions of the dienyl complex **Ia** and the appropriate amino acid ester nucleophile were mixed in molar ratios varying between 1:0.25 and 1:5. The IR spectrum of each of the equilibrium reaction mixtures was recorded at ambient temperature between 2200 and 1900 cm^{-1} using a Pye-Unicam SP3-200 spectrophotometer and matching 0.5 mm CaF_2 cells.

TABLE 3. *In situ* chiral discrimination in the reaction of amino acid esters with rac. $(2R,2S)$-$[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]BF_4$ in CD_3CN

$H_2N-\underset{H}{\overset{R}{C}}-CO_2Et$ [a]	Diastereomer ratio	Diastereomeric excess (d.e.)
$R = CH_3$	54/46	8
$R = CHMe_2$	56/44	12
$R = CH_2OH$	56/44	12
$R = Ph$	43/57	14

[a] (*S*)-Enantiomer of amino acid ester employed except for R = Ph where the (*R*)-enantiomer used.

2.6. NMR studies

The ^1H NMR spectra of the cationic adducts **II** were recorded on a 400 MHz JEOL GX400 spectrophotometer. The chiral discrimination in the reaction of racemic **Ia** with various optically active amino acid esters was measured quantitatively in CD_3CN by ^1H NMR spectroscopy using a 360 MHz Bruker WM 360 spectrometer. [Fe] = 0.07 mol dm^{-3} was employed and [Fe]/[amino acid ester] ratios of 2–10:1. Under these conditions, the species predominantly present are unchanged **Ia** and the cationic adducts $[Fe(CO)_3(RNH_2 \cdot C_6H_6OMe)]^+$. Proton assignments were made on the basis of spin decoupling experiments and by analogy with data for related systems. Product diastereomer ratios were determined by integrating pairs of diastereomer signals. The values quoted are averages obtained using several diene ring protons as well as nucleophile alkyl signals (see Table 2).

2.7. Mass spectrometry studies

Fast atom bombardment (FAB) mass spectra of representative cationic and neutral adducts **II** and **III** were recorded on a VG Analytical MM 12-12 quadrupole mass spectrometer fitted with a VG Analytical FAB ion source. This instrument incorporates an Ion-Tech. Ltd. Model B11 NF fast-atom gun. Both positive and negative ion spectra were measured up to m/z 600 using 3-nitrobenzylalcohol as matrix.

2.8. Kinetic studies

The kinetics of the rapid reactions of the dienyl complexes **Ia** and **Ib** with each of the amino acid esters in acetonitrile were studied by use of a thermostatted stopped flow spectrometer. Signals from the photomultiplier detector were logged and passed through a Techmas A/D converter (A211, module 6812) and thence to an Apple II Europlus microcomputer. Data acquisition was carried out using the DASH program (data acquisition short half-life) described elsewhere [12]. This program is written in Apple soft BASIC and

operates a machine-code subroutine that collects and stores the data within the computer memory. A total of 1000 data points are collected at regular intervals throughout the total collection time chosen.

All the processes were monitored at 380 nm, where a large decrease in absorbance occurs during reaction. Use of a large excess of nucleophile ([Fe] = (0.5–1.4) × 10^{-3} mol dm^{-3}, [amino acid ester] ≥ (6–100) × 10^{-3} mol dm^{-3}) ensured that pseudo-first-order conditions prevailed, and that the neutral deprotonated adduct was the final product in each reaction. Pseudo-first-order rate constants, k_{obs}, were calculated from the slopes of plots of $\log(A_t - A_\infty)$ *versus* time, using the KOBS program previously described [12]. Such kinetic plots were generally linear for at least two half-lives. Each k_{obs} value reported is the average of at least triplicate runs, having an average reproducibility of ±5%. Second-order rate constants, k_1, were calculated from a least squares analysis of k_{obs} *versus* [nucleophile] plots, the errors quoted being the standard errors of estimate of these analysis.

Enthalpies of activation were calculated from a least-squares fit to the Arrhenius equation for runs carried out at different temperatures while maintaining [nucleophile] constant. Errors quoted are the standard errors of estimate for these analyses. Entropies of activation were calculated by standard procedures from the second-order rate constants, k_1.

3. Results and discussion

3.1. Nature of the reactions

Addition of amino acid esters to the dienyl iron cations **I** in CH_3CN occurs in two steps, as depicted in Scheme 1. Depending on the [amino acid ester]/[Fe] ratio employed, either the cationic adducts **II** or the neutral adducts **III** are obtained, or a mixture of both. This is clearly shown from the IR spectral data in Fig. 1, where $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6]BF_4$ (**Ia**) (10^{-2} mol dm^{-3}) has been mixed with varying amounts of alanine ethyl ester. At low [amino acid ester]/[Fe] ratios (0.5–1.5 : 1), the ν(CO) bands observed can be assigned to unchanged dienyl salt (2120, 2066 cm^{-1}) and the cationic adduct **IIc** (2066, 1988 cm^{-1}). With a large excess (≥ 4-fold) of alanine ethyl ester (or the addition of a drop of Et_3N), the only ν(CO) bands observed (2056, 1981 cm^{-1}) are those assigned to the neutral adduct **IIIc**. These latter bands are typical of neutral tricarbonyl (diene) iron complexes, such as the related anilino adducts [12].

At intermediate [alanine ethyl ester]/[Fe] ratios, mixtures of **Ia, IIc** and **IIIc** are observed. This confirms the equilibrium nature of reaction (1), as shown in Scheme 1. The spectroscopic results in Fig. 1 indicate a relatively large pseudo-equilibrium constant for initial cationic adduct formation (K_1 *ca.* 10^3), while the equilibrium constant K_2 for the subsequent deprotonation to yield the neutral adduct is several hundred times smaller.

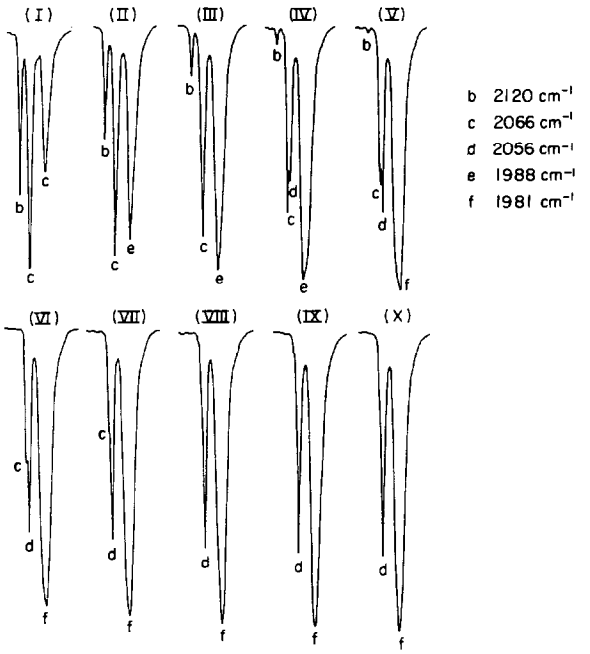
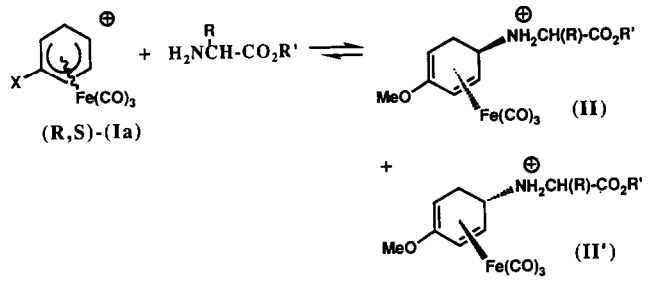


Fig 1. IR spectra of mixtures of cation (**Ia**, 10^{-2} mol dm^{-3}) with alanine ethyl ester in CH_3CN. [ala OEt]/[Fe] ratios: (I) 0.5:1; (II) 1:1; (III) 1.5:1; (IV) 2:1; (V) 2.5:1; (VI) 3:1′ (VII) 3.5:1; (VIII) 4:1; (IX) 5:1; (X) 8:1.

Analogous two-stage equilibria were similarly demonstrated by IR spectroscopy for the addition of each of the amino acid esters to cations **Ia** and **Ib** (Table 1). In all cases, adduct formation could be quantitatively and rapidly reversed by the addition of trifluoroacetic acid to the reaction mixtures.

The nature of reactions (1) was also confirmed from *in situ* ^1H NMR spectral studies in CD_3CN. In several cases, the cationic and neutral adducts were also isolated and characterized by elemental analysis and FAB mass spectrometry (see Experimental section). The ^1H NMR spectra of the cationic **II** and neutral **III** adducts (Experimental section and Table 2) are fully consistent with tricarbonyl (substituted −1,3-diene) iron species, and are very similar to those previously reported [12,13] for related anilino adducts. On the basis of the small $J_{5',6}$ coupling constants (3.1–3.3 Hz) shown in Table 2, an exo configuration can be assigned to the amino acid ester group attached to the C(5) atom of the diene ring in adducts **II**. Examination of molecular models would predict [14] much larger $J_{5',6}$ coupling constants (*ca.* 11 Hz), on the basis of Karplus angles, for the alternative



Scheme 2.

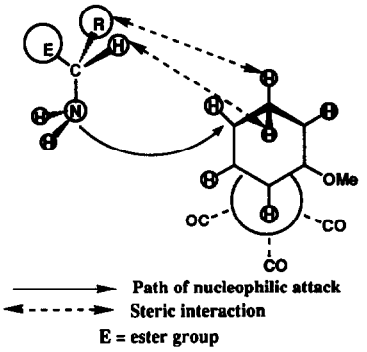


Fig. 2. Approach of (*R*)-alanine ethyl ester to the (2*S*) hand of **Ia**.

endo configuration. This exo product stereochemistry provides strong support for direct nucleophilic addition of the amino acid esters to the side of the dienyl ring of cations **I** remote from the $Fe(CO)_3$ moiety.

Because of the equilibrium nature of reactions **1**, isolation of pure samples of the cationic adducts **II** was difficult (see Experimental section). However, the neutral adducts were readily isolated from reaction mixtures containing an excess of base. The most convenient procedure involved passing ammonia gas through equimolar mixtures of the dienyl salt **I** and amino acid ester in CH_3CN.

3.2. Chiral discrimination in reaction (1)

The dienyl cation $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ (**Ia**) possesses planar chirality. In previous studies [15–17], we have shown that optically active phosphorus and amine nucleophiles can discriminate between the two enantiomeric forms of racemic (2*R*, 2*S*)-(**Ia**).

The extent of chiral discrimination in reactions (1, X = MeO) has been determined here from *in situ* ^1H NMR spectral studies in CD_3CN (Tables 2 and 3). Under the conditions employed in these experiments ([Fe]/amino acid ester] $\geq 2:1$), the only species present at equilibrium are unchanged dienyl salt **Ia** and the diastereomeric pair of cationic adducts **II** (Scheme 2). In each each case, except for phenylglycine, the (*S*)-form of the amino acid ester was used.

Chiral discrimination, as determined from the ratio of the diastereomeric adducts {**II**/**II**'}, is seen to be quite low in these systems (Table 3). The diastereomeric excess (d.e. *ca.* 8%) in the reaction of alanine ethyl ester with **Ia** is similar in magnitude to that previously noted [17] in the related attack of (*R*)-1-phenylethylamine on **Ia**. Models suggest that the major source of this discrimination arises from differential steric interaction between the methylene group of the two hands of the dienyl salt **Ia** and the substituent groups (R, CO_2Et) of the attacking amino acid ester (Fig. 2). Support for this hypothesis comes from the modest increase in chiral discrimination when the bulk of the amino acid substituent R is increased (Table 3; *e.g.* d.e. *ca.* 14% for phenylglycine).

The extent of chiral discrimination in reactions (1) is independent, within experimental error ($\pm 2\%$), of the ratio in which the reagents are mixed ([Fe]/[amino acid ester] ratios of 2–10:1 employed). This suggests that the discrimination is thermodynamic in origin, depending on the relative energies of the two diastereomeric adducts **II** and **II**'.

The modest chiral discrimination provides a simple method for the preparation of optically active **Ia**, albeit in low optical purity. Reaction between racemic **Ia** and amino acid esters in CH_3CN using a [Fe]/[amino acid ester] ratio of *ca.* 2:1, followed by addition of diethyl ether, allowed the ready recovery of excess unchanged dienyl salt (see Experimental section). With the (*S*)-amino acid esters, comparison of the circular dichroism spectra of the recovered dienyl salts with that reported previously [17] for the fully resolved complex, confirmed that the (2*S*)-$[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeOC_6H_6)]^+$ enantiomer is present in excess (Table 4). That is, during reactions (1) the (*S*)-amino acid ester nucleophiles react preferentially with the (2*R*)- hand of the dienyl cation **Ia**. The reverse is observed with (*R*)-phenylglycine as nucleophile (Table 4).

The enantiomeric excess obtained in these synthetic experiments in somewhat lower than the discrimination found *in situ* (Table 3). Similar behaviour was previously noted in earlier studies with phosphine nucleophiles [15,16] and may reflect redistributions in the equilibrium systems caused by the addition of diethyl ether.

TABLE 4. Optical purity of recovered **Ia** from chiral discrimination experiments

Nucleophile employed	% optical purity of recovered (**Ia**)	Enantiomer in excess
S-Alanine ethyl ester	2	*S*
S-Valine ethyl ester	3.5	*S*
R-Phenylglycine ethyl ester	4	*R*

3.3. Kinetics and mechanisms

Under the conditions employed in the present kinetic studies, each of the reactions (1) proceeds to completion; *i.e.* the last deprotonation step in Scheme 1 may be regarded as effectively proceeding only to the right (k_{-2} may be neglected).

Kinetic results for reactions (1) with cations **Ia** and **Ib** with several amino acid esters at various tempera-

TABLE 5. Kinetic results for the addition of amino acid esters to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}5\text{-}C_6H_7)]^+$ (**Ib**) in CH_3CN

Nucleophile	Temperature (°C)	10^2 [Nuc] (mol dm^{-3})	k_{obs} (s^{-1})	k_1 (mol^{-1} dm^3 s^{-1})
$H_2NCH(Me)CO_2Et$ [a]	0.0	1.00	48.7	
		1.20	55.4	
		1.60	65.7	3330 (360)
		1.80	69.4	
		2.00	73.8	
		2.60	105	
	1.0	0.36	18.5	
	6.0	0.36	23.2	
	12.0	0.36	25.8	
	15.0	0.36	28.7	
	20.0	0.36	32.6	
	25.0	0.36	35.5	
	28.0	0.36	40.4	
	39.0	0.36	46.5	
	43.0	0.36	55.9	
	45.0	0.36	60.6	
$H_2NCH(CH_2Ph)CO_2Me$ [b]	0.0	0.60	20.8	
		1.00	30.0	
		1.70	50.6	2860 (170)
		2.00	64.1	
		2.60	75.5	
	6.0	1.00	34.2	
	8.0	1.00	37.3	
	12.0	1.00	39.7	
	15.0	1.00	43.2	
	22.0	1.00	51.5	
	30.0	1.00	61.8	
	35.0	1.00	69.9	
	47.0	1.00	88.6	
$H_2NCH(Ph)CO_2Et$ [c]	0.00	0.70	27.8	
		1.00	38.2	3200 (110)
		1.50	52.2	
		1.70	59.0	
	5.0	0.324	12.3	
	9.0	0.324	14.7	
	13.0	0.324	17.6	
	18.0	0.324	19.8	
	24.0	0.324	22.6	
	29.0	0.324	27.5	
	34.0	0.324	30.7	
	48.0	0.324	45.4	
$H_2NCH(CHMe_2)CO_2Et$ [d]	0.0	0.70	29.7	
		0.80	32.0	
		1.00	37.6	3740 (290)
		1.40	52.2	
		1.60	64.0	

[a] At 0.0°C, [Fe] = 1.20×10^{-3} mol dm^{-3}; at other temperatures [Fe] = 8.0×10^{-4} mol dm^{-3}. [b] At 0.0°C, [Fe] = 1.18×10^{-3} mol dm^{-3}; at other temperatures [Fe] = 1.04×10^{-3} mol dm^{-3}. [c] At 0.0°C, [Fe] = 1.15×10^{-3} mol dm^{-3}; at other temperatures [Fe] = 5.0×10^{-4} mol dm^{-3}. [d] [Fe] = 1.01×10^{-3} mol dm^{-3}.

TABLE 6. Kinetic results for the addition of amino acid esters to $[Fe(CO)_3(1\text{-}5\text{-}\eta\text{-}2\text{-}MeO\ C_6H_7)]^+$ (**Ia**) in CH_3CN

Nucleophile	Temperature (°C)	10^2 [Nuc] (mol dm^{-3})	k_{obs} (s^{-1})	k_1 (mol^{-1} dm^3 s^{-1})
$H_2NCH(Me)CO_2Et$ [a]	0.0	1.20	7.5	
		1.39	8.9	
		1.60	9.3	
		1.80	13.1	
		2.00	13.6	666 (34)
		2.30	15.0	
		2.60	17.4	
		3.20	21.7	
		3.80	24.2	
	2.0	1.39	10.1	
	6.0	1.39	11.7	
	9.0	1.39	14.0	
	13.0	1.39	16.0	
	16.0	1.39	17.4	
	20.0	1.39	20.8	
	24.0	1.39	24.2	
	30.0	1.39	26.9	
	34.0	1.39	36.1	
$H_2NCH(CH_2Ph)CO_2Me$ [b]	0.0	0.90	4.7	
		1.10	5.0	
		1.40	6.4	
		1.70	8.6	651 (38)
		1.80	9.1	
		2.00	11.2	
		2.30	13.3	
		2.60	15.1	
	10.0	1.55	8.5	
	15.0	1.55	10.1	
	19.0	1.55	11.8	
	23.0	1.55	13.7	
	26.0	1.55	15.1	
	28.0	1.55	17.0	
	33.0	1.55	19.8	
	43.0	1.55	27.9	
	50.0	1.55	35.4	
$H_2NCH(Ph)CO_2Et$ [c]	0.0	1.00	5.9	
		1.50	8.9	
		1.70	11.7	
		2.40	14.9	649 (35)
		2.80	16.6	
		3.30	19.7	
		3.70	23.6	
		3.80	25.4	
	3.0	0.54	2.0	
	8.0	0.54	2.7	
	12.0	0.54	3.6	
	17.0	0.54	4.2	
	21.0	0.54	5.0	
	25.0	0.54	5.5	
	30.0	0.54	5.9	
	36.0	0.54	8.6	
	41.0	0.54	9.7	

Table 6 (continued)

Nucleophile	Temperature (°C)	10^2 [Nuc] (mol dm^{-3})	k_{obs} (s^{-1})	k_1 (mol^{-1} dm^3 s^{-1})
$H_2NCH(CHMe_2)CO_2Et$ [d]	0.0	1.30	8.2	
		1.40	9.1	
		1.70	9.3	
		2.07	10.8	
		2.40	14.3	
		3.00	19.0	
		3.50	19.5	569 (13)
		4.10	22.7	
		4.70	29.9	
		6.00	35.4	
		7.10	41.1	
		7.50	43.1	
		9.80	55.5	
	5.0	2.07	11.7	
	11.0	2.07	17.9	
	16.0	2.07	20.1	
	21.0	2.07	24.0	
	25.0	2.07	30.5	
	35.0	2.07	38.7	

[a] [Fe] = 1.41×10^{-3} mol dm^{-3}. [b] At 0.0°C, [Fe] = 1.32×10^{-3} mol dm^{-3}; at other temperatures [Fe] = 1.16×10^{-3} mol dm^{-3}. [c] At 0.0°C, [Fe] = 1.32×10^{-3} mol dm^{-3}; at other temperatures [Fe] = 8.0×10^{-4} mol dm^{-3}. [d] [Fe] = 1.32×10^{-3} mol dm^{-3}.

tures and amine concentrations are summarized in Tables 5 and 6. In each case, k_{obs} obeys the simple eqn. (1), indicating the bimolecular rate law (2).

$$k_{obs} = k[RNH_2] \quad (1)$$

$$\text{Rate} = k[Fe][RNH_2] \quad (2)$$

This kinetic behaviour is analogous to that we observed previously [18] for the related additions of 4-methylaniline to cations **Ia, Ib**. It may be similarly rationalized in terms of the mechanism outlined in Scheme 1. On the assumption of a steady state concentration for the intermediates **II** (and that k_{-2} is negligible), this scheme leads to the general expression (3). Provided $k_2[RNH_2] \gg k_{-1}$, this equation simplifies to the observed rate law (1, 2) in which the calculated second-order rate constants k refer to the initial ring-addition step, k_1. The assumption of rapid proton removal (k_2) from intermediates **II** is not unreasonable since the Fe(diene)(CO)$_3$ moiety is known [19] to be an electron-withdrawing group.

$$k_{obs} = k_1 k_2 [RNH_2]^2 / (k_{-1} + k_2[RNH_2]) \quad (3)$$

The considerably slower (5–6 times) reactions observed for the 2-MeO-substituted dienyl cation **Ia** with amino acid esters compared with those for the parent cation **Ib** (Tables 5, 6) support direct nucleophilic addition (k_1) to the dienyl rings. Similar differences in reactivity of these two dienyl salts towards other amine, phosphine, and pyridine nucleophiles have been previously reported [20], and rationalized on the basis of INDO molecular orbital calculations [21]. Bimolecular addition to cations **I** is also supported by the large negative entropies of activation ($\Delta S^{\ddagger} = -103$ to -128 J K^{-1} mol^{-1}) calculated for each of the reactions (1)

TABLE 7. Rate and activation parameters for the reaction of amino acid esters with [Fe(CO)$_3$(1-5-η-dienyl)]$^+$ cations in CH_3CN

Dienyl	Nucleophile	k (0°C) (mol^{-1} dm^3 s^{-1})	$\Delta H^{\ddagger}$ (kJ mol^{-1})	$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})
C_6H_7	$H_2NCH(Me)CO_2Et$	3330	15.4 (0.6)	−124 (4)
	$H_2NCH(CH_2Ph)CO_2Me$	2860	14.8 (0.3)	−128 (4)
	$H_2NCH(Ph)CO_2Et$	3200	19.4 (0.8)	−111 (6)
	$H_2NCH(CHMe_2)CO_2Et$	3740		
2-$MeOC_6H_6$	$H_2NCH(Me)CO_2Et$	666	25.3 (1.4)	−105 (10)
	$H_2NCH(CH_2Ph)CO_2Me$	651	24.6 (0.7)	−109 (4)
	$H_2NCH(Ph)CO_2Et$	649	26.0 (0.8)	−103 (6)
	$H_2NCH(CHMe_2)CO_2Et$	569	24.2 (1.9)	−110 (14)

(Table 7). The relatively small enthalpies of activation (Table 7) are similar to those found for additions of other amines to cations **I** [12,20].

An alternative explanation for the observed rate law can be given in terms of a pre-equilibrium mechanism, *i.e.* by assuming that k_1 in Scheme 1 is very much faster than k_2. This mechanism predicts the general expression (4). Provided $K_1[RNH_2] \gg 1$, this simplifies to eqn. (5), which is consistent with the observed rate law. In this case the calculated second-order rate constants k refer to the deprotonation step, k_2 (rather than ring addition).

$$k_{obs} = k_2 K_1 [RNH_2]^2 / (1 + K_1[RNH_2]) \quad (4)$$

$$k_{obs} = k_2 [RNH_2]$$

The condition $K_1[RNH_2] \gg 1$ is likely to be met under the kinetic conditions employed, since IR measurements indicate pseudo-equilibrium constants K_1 of *ca.* 10^3. It is not possible at this stage to distinguish unequivocally between these two alternative mechanisms.

However, on the assumption that the former steady state mechanism applies, the present kinetic data will allow amino acid esters to be placed in the quantitative nucleophilicity order recently established [22] for some 40 nucleophiles towards cation **Ib**. Of particular interest is a comparison with other representative amine nucleophiles shown in Table 8. Alanine ethyl ester is seen to be somewhat less nucleophilic than imidazole, but more reactive than pyridine and aniline. However, a significant feature for the amine nucleophiles in Table 8 is the relatively small variation in k despite quite large changes in nucleophile basicity. In earlier studies [12] with a series of substituted anilines, marked variations in the rate of ring addition were observed with changes in nucleophile basicity (Brønsted slope $\alpha = 1.0$)

TABLE 8. Relative nucleophilic reactivities of amines towards cation **Ib** at 0°C in CH_3CN

Nucleophile	k (mol^{-1} dm^3 s^{-1})	rel k	pK_a (H_2O)	Ref.
Imidazole	4390	2.2	6.95	20
Alanine ethyl ester	3330	1.7	7.7	This work
Pyridine	2170	1.1	5.23	23
Aniline	2000	1	4.63	12
Phenylglycine ethyl ester	3200	1.6		This work

Acknowledgements

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