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Optically active transition-metal complexes. III. Synthesis of optically active (η^4-aminodiolefin)tricarbonyl iron complexes. Kinetic resolution of a chiral amine by means of an optically active dienyl iron cation ☆

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Abstract

The synthesis of optically active η^4-(aminodiolefin)tricarbonyl iron complexes by the nucleophilic addition of primary and secondary amines to the optically active tricarbonyl-(*1R*)-(η^5-methyl-nopadienyl)iron(1 +) cation (**4**) is described. Under either kinetic or thermodynamic control, the reaction leads to (*E,Z*)- or (*E,E*)-diolefin complexes with generation of a new chiral carbon centre. Racemic (*R/S*)-phenylethylamine was kinetically resolved (*de* = 38%) by treatment with **4** at −78°C.

Keywords: Optically active ligands; Iron; Carbonyl complexes; Kinetic resolution.

1. Introduction

There has been considerable recent interest in the synthesis and reactivity of η^5-tricarbonyl(pentadienyl)-iron(1 +) complexes. Their utility as intermediates and reactands in organic synthesis with respect to highly diastereoselective addition reactions of various nucleophiles to η^5-tricarbonyl(dienyl)iron(+1) cations is well documented [1]. The U-shaped cationic complex **II**, synthesized from the corresponding alcohol complex **I** (LG = H), reacts with a wide range of nucleophiles such as alcohols, amines, carbon nucleophiles, hydrides, phosphites and phosphines in a stereoselective but not always regioselective manner, giving rise to four possible regiochemical isomers **IV–VII**. The ratios of the kinetically controlled (*E,Z*)- and thermodynamically controlled (*E,E*)-complexes depend on the electronic and steric effects of R^1, R^2 and R^3 as well as the type of nucleophile employed [1e,1k,2]. Recently, several groups have reported on a regio- and stereospecific nucleophilic substitution via S-shaped cationic complexes such as **IIIb** to give (*E,E*)-complexes of the form **VI**. However, this route is limited to specific leaving groups LG, as well as carbon nucleophiles and phosphorus nucleophiles such as phosphites [3] (Scheme 1).

In all cases, however, the nucleophile invariably attacks trans to the tricarbonyl iron moiety [1–3]. We have recently prepared the optically active tricarbonyl-(*1R*)-(η^5-methylnopadienyl)iron(1 +) cation **4**, derived from the optically active natural product (*1R*)(-)-myrtenal via the ketone **1** [4] (Scheme 2).

The cation offers various advantages over the previously discussed pentadienyl complexes:

(a) Owing to the optical activity originating from the organic precursor and the planar chirality introduced by coordination of the $Fe(CO)_3$ moiety, nucleophilic reactions will generate a new chiral centre, whose enantiomeric purity is easily checked by NMR spectroscopy,

(b) Because of the ring structure, a nucleophile will only attack at C12 of the dienyl system, limiting the number of possible products to one pair of (*E,Z*)- and (*E,E*)-diastereomers. By careful kinetic or thermodynamic control of the reaction conditions, it should be possible to generate one single product with a well-defined new centre of chirality.

We have therefore investigated the reaction of complex **4** with a variety of amines and phosphines in order to synthesize optically active organometallic amines and

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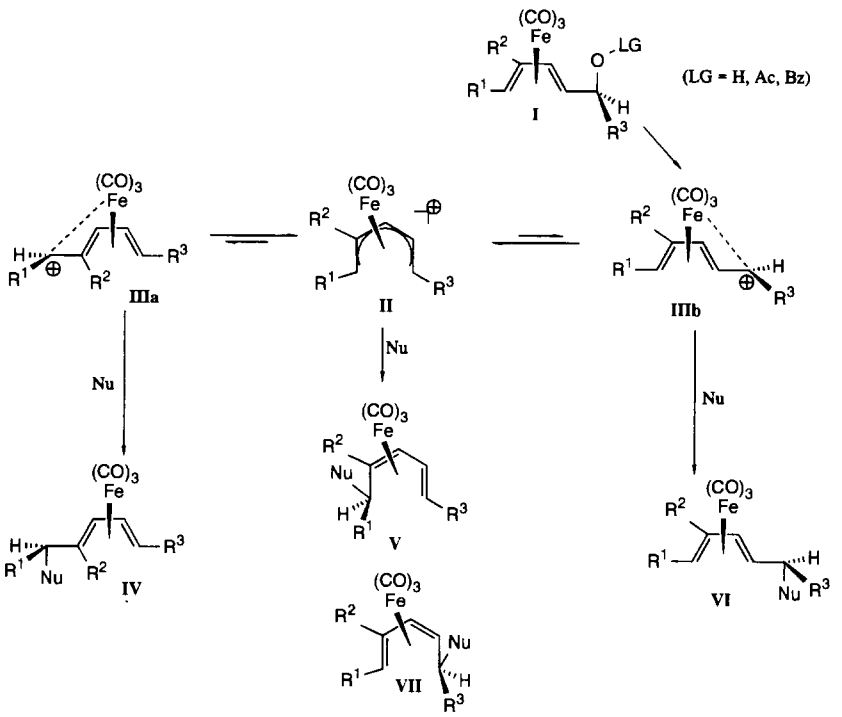


Scheme 1.

phosphines, which might themselves be useful as ligands in homogeneous catalysis or might be suitable as derivatizing agents in racemic resolutions.

2. Results and discussion

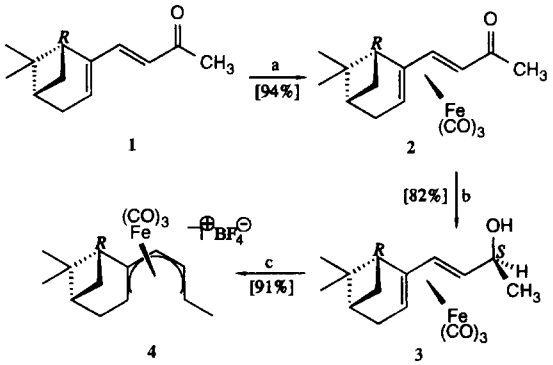
2.1. Reactions between 4 and primary and secondary amines

The (aminodiene)tricarbonyl iron complexes were prepared as outlined in Scheme 3. They were obtained in good to excellent yields (Table 1). We used two general methods:

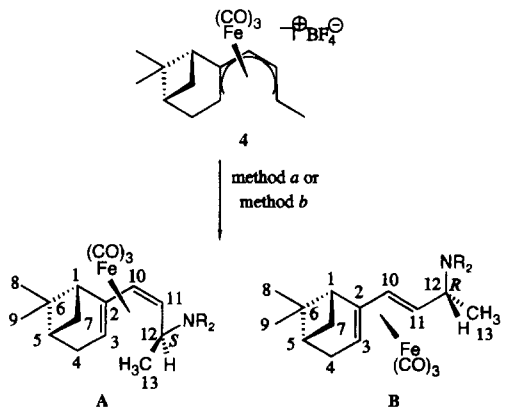
(a) Addition of two equivalents of the primary or secondary amine to **4** at −78°C, and

(b) Addition of one equivalent of the amine at room temperature and deprotonation of the primarily formed ammonium salt with a non-nucleophilic base such as NEt_3.

Absolute configurations of the products were assigned in analogy to previous work by Maglio et al. [1o] as well as our own X-ray structure analysis of an addition product with a secondary phosphine [5]. (*E,Z*)- and (*E,E*)-diolefin complexes are easily distinguished by their typical chemical-shift values in ^1H and ^{13}C NMR. Typical values in the ^1H NMR for H11 in (*E,Z*)- and (*E,E*)-diolefin complexes are at 1.9–2.5 ppm and 0.6–1.1 ppm respectively [1o]. Table 1 shows that method (a) in most cases led to the kinetically controlled (*E,Z*)-diolefin complexes **A** only, while method



Scheme 2. (a) $Fe_2(CO)_9$ (1.5 eq), benzene 18 h, 80°C; (b) $NaBH_4$ (2.3 eq), MeOH, 1.5 h, 0°C; (c) HBF_4, propionic anhydride, 0.5 h, 0°C.



Scheme 3.

Table 1
The reaction between the optically active cation complex **4** and primary or secondary amines

Amine	Product (method)	A [a]	B [a]	(%)	T (°C)	t (h)	eq
Dimethylamine	**5** (a)	100	–	88	−78	4	2.2
Dimethylamine	**5** (b)	90	10	80	r.t.	72	1.1
Diethylamine	**6** (a)	100	–	97	−78	1.5	2.2
Diethylamine	**6** (b)	–	100	65	r.t.	84	1.1
Piperidine	**7** (a)	100	–	91	−78	4	2.2
Piperidine	**7** (b)	89	11	79	r.t.	72	1.1
Cyclohexylamine	**8** (b)	12	88	51	r.t.	72	1.1
Isopropylamine	**9** (b)	11	89	46	r.t.	72	1.1
Aniline	**10** (a)	–	100	85	−78	4	2.2
o-Toluidine	**11** (a)	–	100	70	−78	13	2.2
Benzylamine	**12** (b)	–	100	88	r.t.	84	1.1

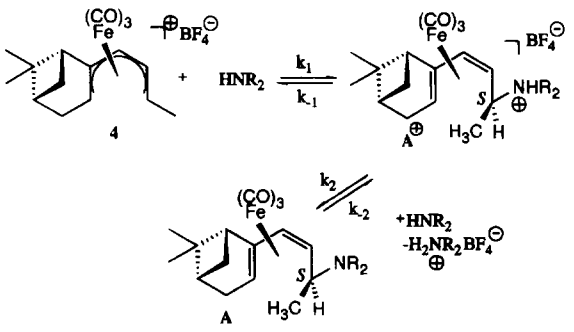
[a] The ratios **A**/**B** are determined by the integration of the ^{1}H NMR spectra.

(b) predominantly gave the thermodynamically more stable (*E*,*E*)-complexes **B** (Scheme 3 and Table 1).

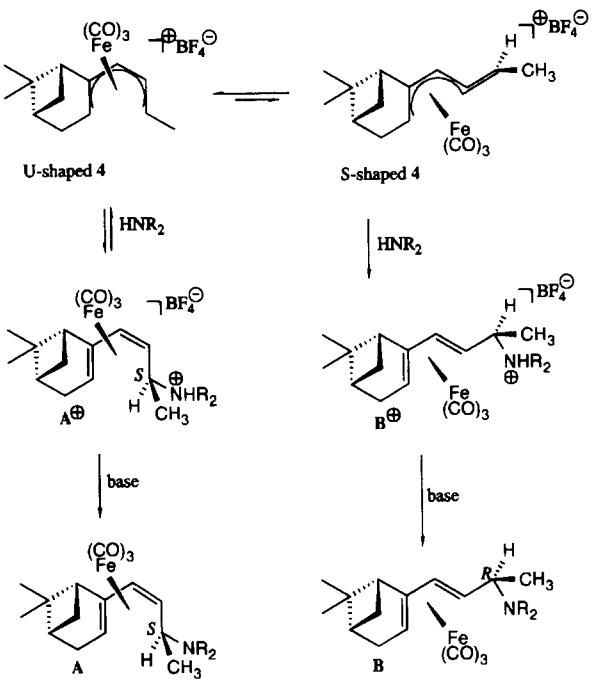
Further conclusions can be drawn from Table 1. The ratio **A**/**B** increases with the basicity of the respective amine on the addition of two equivalents of amine. This is probably due to the fact that the second amine rapidly deprotonates the primarily formed ammonium salt. This is the case for strongly basic amines such as dimethylamine, diethylamine and piperidine (Scheme 4).

The addition of the first amine is therefore irreversible ($k_2 \gg k_{-1}$, and k_{-2} negligible) in these cases. For dimethylamine and piperidine, it was not possible under any conditions to generate exclusively the (*E*,*E*)-diolefin complex **B**. With the bulkier diethylamine, however, the reaction via method (b) gave full conversion to the (*E*,*E*)-diolefin **B**. This means that the U-shaped cation **II** and the S-shaped cation **IIIb** can still achieve equilibrium, so that the thermodynamically more stable (*E*,*E*)-diolefin product can be formed eventually. A reaction time of several days may be necessary in some cases to establish this equilibrium fully, with the exclusive formation of product **B**.

While the reactions in some cases led to almost quantitative yields, the yields decreased with longer reaction times and at ambient temperatures. This is due



Scheme 4.



Scheme 5.

to some decomposition of the cationic precursors as well as competing elimination reactions of **4** with formation of a mixture of triolefin complexes (10–20% isolated yields). Based on the observed results, the detailed kinetic studies of nucleophilic addition reactions by Kane-Maguire and co-workers [6], and ^{1}H NMR studies on the equilibria between U- and S-shaped dienyl cations by Sorensen and Jablonski [7], we propose the following reaction mechanism for the nucleophilic addition of primary and secondary amines to the optically active tricarbonyl(η^5-methylnopadienyl)iron cation **4** (Scheme 5):

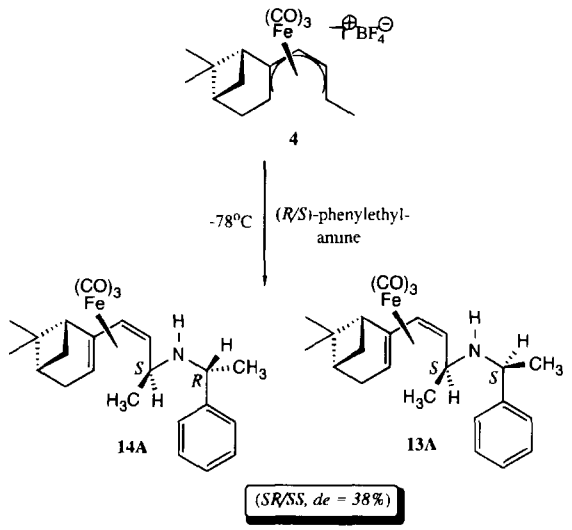
2.2. *Kinetic resolution of (R,S)-phenylethylamine by reaction with 4*

Reaction of **4** with either (*R*)- or (*S*)-phenylethylamine by method (c) (addition of **4** to one or two equivalents of amine at −78°C) gave rise to similar results to those discussed previously (Table 2).

Table 2
The reaction between the optically active cation complex **4** and phenylethylamine

Amine	Product (method)	A	B	(%)	(T) (°C)	t (h)	eq
(*S*)-Phenylethylamine	**13** (b)	–	100	94	r.t.	96	1.1
(*S*)-Phenylethylamine	**13** (c)	100	–	53	−78	8	1.1
(*R*)-Phenylethylamine	**14** (c)	100	–	54	−78	8	1.1
(*R*/*S*)-Phenylethylamine [a]	**13**/**14** (b)	–	100	90	r.t.	72	1.1
(*R*/*S*)-Phenylethylamine	**13**/**14** (c)	100	–	48	−78	2.5	2.2

[a] The ratio **13**/**14** is determined by the integration of the ^{1}H NMR spectra.



Scheme 6.

Reaction at low temperatures led to the (*E,Z*) product only, while reaction at ambient temperatures gave the rearranged (*E,E*) product. The pure (*E,Z*) product could only be isolated by strictly keeping the reaction mixture at −78°C and deprotonating the intermediate ammonium salt with the non-nucleophilic base $EtN(^iPr)_2$, as the rearranged product **B** begins to form at −50°C. Reaction of optically active **4** with racemic (*R,S*)-phenylethylamine by method (b) led to an equal mixture of the (*E,E*)-complexes **13B** and **14B**, differing only in the chirality of phenylethylamine. No kinetic resolution was therefore observed under these conditions. **13B** and **14B** could not be separated by chromatography. This changed when **4** was added at −78°C to two equivalents of (*R,S*)-phenylethylamine in methylene chloride. After deprotonation with $EtN(^iPr)_2$ at −78°C, the amines **13A** and **14A** were isolated and could be separated by chromatography. The ratio of **13A** to **14A** was determined as 1:2.2 (*de* = 38%). The optically active **4** had therefore preferentially reacted with (*R*)-phenylethylamine. This to our knowledge constitutes the first example of a kinetic resolution of a racemic amine with an optically active dienyl complex (Scheme 6).

The addition of (*R/S*)-phenylethylamine to the optically active **4** (method (a)), however, led to a considerable decrease in the diastereomeric excess (1:1.3; *de* = 13%).

We are currently examining whether optically pure (*R*)-phenylethylamine can be separated from the complex and the starting material **4** recovered, so that it can be used for repeated resolutions. We are also investigating whether other chiral amines can be resolved in a similar manner. Analogous reactions to those described in this paper can also be performed with secondary phosphines. These will be reported in a separate paper [5].

3. Experimental details

All experiments were carried out under an atmosphere of nitrogen using solvents purified under nitrogen by standard procedures. The starting optically active cation **4** was prepared as described in the literature [4]. Mass spectra were recorded on a Finnigan MAT 95 instrument. IR spectra were recorded on a Perkin–Elmer 1720 X infrared spectrophotometer and NMR spectra on Varian VXR 300 and Varian Unity 500 instruments. ^{13}C NMR spectra were assigned by use of APT and were decoupled. Tetramethylsilane was used as internal standard in the case of C_6D_6. In the case of $CDCl_3$, the chemical shifts are referred to the signal of solvent.

3.1. Preparation of the amine complexes

3.1.1. Method (a)

The amine (2.2 eq) was added in one portion to a solution of the optically active cation **4** in methylene chloride (10–40 ml) at room temperature or −78°C. The reaction mixture was stirred for 1.5–48 h. The solvent was evaporated and the residue was purified by chromatography (SiO_2).

3.1.2. Method (b)

The amine (1.1 eq) was added in one portion to a solution of the optically active cation **4** in methylene chloride (10–30 ml) at room temperature. The reaction mixture was stirred for 84–96 h. The primarily formed ammonium salt was deprotonated with NEt_3 (1.1 eq) at room temperature. The solvent was evaporated and the residue was purified by chromatography (SiO_2).

3.1.3. Method (c)

The optically active cation **4** in methylene chloride (20.0 ml) was slowly added to phenylethylamine (1.1 or 2.2 eq) in methylene chloride (30.0 ml) at −78°C within 0.5 h. The reaction mixture was stirred for 2.5–8 h at −78°C. The primarily formed ammonium salt was deprotonated with $EtN(^iPr)_2$ (1.2 eq) at −78°C. The solvent was evaporated and the residue was purified by chromatography (SiO_2).

3.2.1. Tricarbonyl[η⁴-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(Z)-(2S)-2-N,N-dimethylamino-but-3-ene]iron (5A)

Method (a); eluent, hexane/ether (3:1) to ether, yellow oil, yield 0.40 g (88%). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.93 (s, 3H, H9), 1.16 (d, *J* = 6.7 Hz, 3H, H13), 1.33 (s, 3H, H8), 1.43 (d, *J* = 10.1 Hz, 1H, H7), 1.80 (dd, *J* = 7.9 Hz, *J* = 10.4 Hz, 1H, H11), 2.05 (s, 6H, $2 \times CH_3(NMe_2)$), 1.94–2.08, 2.15–2.22, 2.50–2.60 (3m, 7H, H1, H3, H4, H5, H7, H12), 5.28 (d, *J* = 7.9 Hz, H10). ^{13}C NMR (125 MHz, $CDCl_3$): δ

(ppm) = 19.26 (C13), 21.23 (C9), 25.05 (C8), 29.12 (C4), 35.94 (C7), 38.95 (C6), 39.09 ($CH_3(NMe_2)$), 41.22, 46.92, 50.05, 52.80 (C1, C3, C5, C11), 56.60 (C12), 81.45 (C10), 125.03 (C2), 211.29 (CO). IR (hexane): ν(C≡O) = 2038, 1974, 1962 cm^{-1}. Anal. Found: C, 60.10; H, 7.01; N, 3.54. $C_{18}H_{25}FeNO_3$ (359.25). Calc.: C, 60.02; H, 7.01; N, 3.89%.

3.2.2. *Tricarbonyl[η⁴-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(Z)-(2S)-2-N,N-diethylamino-but-3-ene]iron (6A)*

Method (a); eluent, hexane/ether (1:1), orange oil, yield 0.39 g (97%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.93 (t, J = 7 Hz, 6H, 2 × CH_3(NEt$_2$)), 1.02 (s, 3H, H9), 1.17 (d, J = 5.8 Hz, 3H, H13), 1.41 (s, 3H, H8), 1.49 (d, J = 9.7 Hz, 1H, H7), 1.97 (br t, 1H, H11), 2.01–2.09, 2.21–2.48, 2.56–2.64 (3m, 11H, H1, H3, H4, H5, H7, H12, 2 × CH_2(NEt$_2$)), 5.27 (d, J = 7.9 Hz, H10). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 15.01 (CH_3(NEt$_2$)), 19.22 (C13), 22.40 (C9), 26.13 (C8), 30.06 (C4), 37.05 (C7), 39.95 (C6), 43.54 (CH$_2$(NEt$_2$)), 42.21, 47.88, 53.79, 54.22, 54.84 (C1, C3, C5, C11, C12), 82.89 (C10), 126.19 (C2), 212.45 (CO). IR (hexane): ν(C≡O) = 2038, 1972, 1961 cm^{-1}. Anal. Found: C, 61.66; H, 7.88; N, 3.21. $C_{20}H_{29}FeNO_3$ (387.30). Calc.: C, 62.00; H, 7.54; N, 3.61%.

3.2.3. *Tricarbonyl[η⁴-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(E)-(2R)-2-N,N-diethylamino-but-3-ene]iron (6B)*

Method (b); eluent, hexane/ether (10:1) to ether, yellow oil, yield 0.30 g (65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 0.46 (t, J = 8.8 Hz, 1H, H11), 0.94 (s, 3H, H9), 1.02 (t, J = 7.0 Hz, 6H, 2 × CH$_3$(NEt$_2$)), 1.15 (d, J = 6.8 Hz, 3H, H13), 1.40 (s, 3H, H8), 1.42–1.50 (m, 2H, H7, H12), 1.59 (br d, 1H, H3), 1.96–2.08, 2.13–2.25, 2.44–2.65 (3m, 9H, H1, H4, H5, H7, 2 × CH$_2$(NEt$_2$)), 5.29 (d, J = 8.8 Hz, H10). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 14.47 (CH$_3$(NEt$_2$)), 17.61 (C13), 21.97 (C9), 26.07 (C8), 29.76 (C4), 37.05 (C7), 40.18 (C6), 43.73 (CH$_2$(NEt$_2$)), 42.50, 47.45, 53.92, 57.54, 58.23 (C1, C3, C5, C11, C12), 84.70 (C10), 116.49 (C2), 213.15 (CO). IR (hexane): ν(C≡O) = 2037, 1972, 1960 cm^{-1}. Anal. Found: C, 60.27; H, 7.53; N, 3.01. $C_{20}H_{29}FeNO_3$ (387.30). Calc.: C, 62.00; H, 7.54; N, 3.61%.

3.2.4. *Tricarbonyl[η⁴-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(Z)-(2S)-2-N-azacyclohexyl-but-3-ene]iron (7A)*

Method (a); eluent, hexane/ether (1:1), orange oil (0.89, 91%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 1.01 (s, 3H, H9), 1.22 (d, J = 6.4 Hz, 3H, H13), 1.35–1.52 (m, 7H, H7, 3 × CH_2(C_5H_{10}N)), 1.41 (s, 3H, H8), 1.91 (br dd, 1H, H11), 2.00–2.10, 2.11–2.29, 2.40–2.50, 2.55–2.65 (4m, 11H, H1, H3, H4, H5, H7, H12, 2 × CH_2(C_5H_{10}N)), 5.33 (d, J = 7.6 Hz, 1H, H10). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 19.65 (C13), 22.46 (C9), 24.92 (CH_2(C_5H_{10}N)), 26.08 (C8), 26.34 (CH_2(C_5H_{10}N)), 30.14 (C4), 36.95 (C7), 39.98 (C6), 49.33 (CH_2(C_5H_{10}N)), 42.25, 47.92, 52.77, 54.16, 58.81 (C1, C3, C5, C11, C12), 82.75 (C10), 125.85 (C2), 212.43 (CO). IR (hexane): ν(C≡O) = 2038, 1973, 1961 cm^{-1}. Anal. Found: C, 62.21; H, 7.35; N, 3.01. $C_{21}H_{29}FeNO_3$ (399.31). Calc.: C, 63.16; H, 7.32; N, 3.50%.

3.2.5. *Tricarbonyl[η⁴-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(E)-(2R)-2-N-phenylamino-but-3-ene]iron (10B)*

Method (a); eluent, CH_2Cl_2, yellow solid, yield 0.55 g (85%); ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.38 (t, J = 8.4 Hz, 1H, H11), 0.91 (s, 3H, H9), 1.34 (d, J = 6.1 Hz, 3H, H13), 1.37 (s, 3H, H8), 1.44 (d, J = 10.4 Hz, 1H, H7), 1.66 (br d, 1H, H3), 1.98–2.06, 2.17–2.25, 2.49–2.62 (3m, 5H, H1, H4, H5, H7), 3.32 (dq, J = 6.4 Hz, J = 7.9 Hz, 1H, H12), 3.52 (s, 1H, NH), 5.29 (d, J = 8.2 Hz, H10), 6.60 (d, J = 7.9 Hz, 2H, 2 × CH(Ph)), 6.71 (t, J = 7.3 Hz, 1H, CH(Ph)), 7.17 (dd, J = 7.3 Hz, J = 8.2 Hz, 2H, 2 × CH(Ph)). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 22.11, 22.64 (C9, C13), 26.01 (C8), 29.79 (C4), 37.10 (C7), 40.10 (C6), 42.40, 47.35, 52.60, 54.40 (C1, C3, C5, C11), 58.97 (C12), 83.10 (C10), 113.86, 117.76 (CH(Ph)), 118.05 (C2), 129.35 (CH(Ph)), 146.95 (C(Ph)), 212.73 (CO). IR (hexane): ν(C≡O) = 2040, 1975, 1963 cm^{-1}. Anal. Found: C, 64.92; H, 6.26; N, 3.33. $C_{22}H_{25}FeNO_3$ (407.28). Calc.: C, 64.87; H, 5.98; N, 3.43%. EI–MS (m/z (rel. int.)): M^+ 407 (1.3), M^+-CO 379 (17.9), M^+-2CO 351 (0.9), M^+-3CO 323 (100), M^+-Fe(CO)$_3$ 267 (6.5).

3.2.6. *Tricarbonyl[η⁴-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(E)-(2R)-2-N-o-tolylamino-but-3-ene]iron (11B)*

Method (a); eluent, CH_2Cl_2, yellow solid, yield 0.25 g (70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) = 0.46 (t, J = 8.4 Hz, 1H, H11), 0.92 (s, 3H, H9), 1.36 (d, J = 6.6 Hz, 3H, H13), 1.38 (s, 3H, H8), 1.44 (d, J = 10.1 Hz, 1H, H7), 1.67 (br d, 1H, H3), 2.11 (s, 3H, CH_3(Ph)), 2.00–2.07, 2.17–2.22, 2.49–2.62 (3m, 5H, H1, H4, H5, H7), 3.39 (m, 2H, H12, NH), 5.26 (d, J = 8.2 Hz, H10), 6.64–6.67, 7.04–7.13 (2m, 4H, 4 × CH(Ph)). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) = 17.69 (C13), 22.09, 22.74 (C9, CH_3C(Ph)), 26.00 (C8), 29.79 (C4), 37.10 (C7), 40.09 (C6), 42.41, 47.36, 52.52, 54.35 (C1, C3, C5, C11), 59.31 (C12), 83.05 (C10), 111.44, 117.35 (CH(Ph)), 117.90 (C2) 122.45 (CH$_3$$C$(Ph)), 127.14, 130.41 ($C$H(Ph)), 145.00 ($C$(Ph)), 212.70 (CO). IR (hexane): ν(C≡O) = 2040, 1975, 1963 cm^{-1}. Anal. Found: C, 65.67; H, 7.19; N, 2.87. $C_{23}H_{27}FeNO_3$ (421.30). Calc.: C, 65.56; H, 6.49; N, 3.32%.

3.2.7. Tricarbonyl[η^4-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(E)-(2R)-2-N-benzylamino-but-3-ene]iron (12B)

Method (b); eluent, hexane/ether (10:1) to ether, orange oil, yield 1.00 g (88%). ^{1}H NMR (300 MHz, C_6D_6): δ (ppm) = 0.13 (t, J = 8.7 Hz, 1H, H11), 0.73 (s, 3H, H9), 1.18 (s, 3H, H8), 1.23 (d, J = 6.4 Hz, 4H, H13, this d obscures the signal of H7), 1.48 (d, J = 10 Hz, 1H, H7), 1.74 (sept, 1H, H3), 1.80–1.88 (m, 2H, H4), 2.21 (br t, 1H, H1), 2.29–2.48 (m, 2H, H5, H12), 3.52 (d, J = 12.8 Hz, 1H, CHHPh), 3.66, J = 13.1 Hz, 1H, CHHPh), 4.90 (dd, J = 8.2 Hz, J = 1 Hz, 1H, H10), 7.06–7.32 (m, 5H, 5 × CH(Ph)). ^{13}C NMR (75 MHz, C_6D_6): δ (ppm) = 21.90 (C9), 23.94 (C13), 25.99 (C8), 29.76 (C4), 37.34 (C7), 40.05 (C6), 42.68, 47.51, 51.71, 54.46, 57.04, 60.98 (C1, C3, C5, C11, C12, C14), 84.14 (C10), 116.94 (C2), 127.13, 128.37, 128.56 (CH(Ph)), 141.29 (C(Ph)), 213.51 (CO). IR (hexane): ν(C≡O) = 2039, 1974, 1961 cm^{-1}. Anal. Found: C, 66.28; H, 6.87; N, 3.03. $C_{23}H_{27}FeNO_3$ (421.32). Calc.: C, 65.57; H, 6.46; N, 3.32. EI–MS (m/z (rel. int.)): M$^+$ 421 (0.07), M$^+$-CO 393 (1.2), M$^+$-2CO 365 (1.2), M$^+$-3CO 337.0 (100), M$^+$-Fe(CO)$_3$ 281.0 (2.4).

3.2.8. Tricarbonyl[η^4-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-ene-2-yl]-(E)-(2R)-2-N-(1S)-(1-phenyl-ethylamino)-but-3-ene]iron (13B)

Method (b); eluent, hexane/ether (10:1) to ether, orange oil, yield 0.49 g (94%). ^{1}H NMR (300 MHz, C_6D_6): δ (ppm) = 0.12 (t, J = 9.5 Hz, 1H, H11), 0.72 (s, 3H, H9), 1.12–1.26 (m, 10H, H7, H8, H13, CH(CH_3)Ph), 1.44 (d, J = 10 Hz, H7), 1.74 (sept, J = 3 Hz, H3), 1.80–1.88 (m, 2H, H4), 2.15 (t, J = 6 Hz, 1H, H1), 2.27–2.43 (m, 2H, H5, H12), 3.70 (q, J = 6.5 Hz, 1H, CH(CH$_3$)Ph), 4.87 (dd, J = 8.5 Hz, J = 1 Hz, 1H, H10), 7.07 (tt, J = 7 Hz, J = 1 Hz, 1H, CH(Ph)), 7.14–7.26 (m, 4H, 4 × CH(Ph)). ^{13}C NMR (75 MHz, C_6D_6): δ (ppm) = 21.98 (C9), 23.18 (C13), 24.82 (CH(CH$_3$)Ph), 25.99 (C8), 29.76 (C4), 37.41 (C7), 39.99 (C6), 42.62, 47.46, 54.06, 54.57, 55.77, 61.79 (C1, C3, C5, C11, C12, CH(CH$_3$)Ph), 84.1 (C10), 117.4 (C2), 126.9, 127.1, 128.6 (CH(Ph)), 146.7 (C(Ph)), 213.52 (CO). IR (hexane): ν(C≡O) = 2038, 1973, 1960 cm^{-1}. Anal. Found: C, 67.25; H, 7.11; N, 3.04. $C_{24}H_{29}FeNO_3$ (435.34). Calc.: C, 66.21; H, 6.71; N, 3.21%. EI–MS (m/z (rel. int.)): M$^+$ 435 (0.01), M$^+$-CO 407 (0.7), M$^+$-2CO 379 (0.6), M$^+$-3CO 351 (100), M$^+$-Fe(CO)$_3$ 295 (6.5).

3.2.9. Tricarbonyl[η^4-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-en-2-yl]-(Z)-(2S)-2-N-(1S)-(1-phenyleth-ylamino)-but-3-ene]iron (13A)

Method (c); eluent, hexane/ether (10:1 to 3:1), yellow-orange oil, yield 0.47 g (53%). ^{1}H NMR (300 MHz, C_6D_6): δ (ppm) = 0.66 (s, 3H, H9), 1.10–1.20 (2d, J = 6.7 Hz, the second d is obscured by the s at 1.16, 9H, H8, H13, CH(CH_3)Ph), 1.46 (d, J = 10.1 Hz, H7), 1.60–1.88, 1.96–2.10, 2.20–2.42 (3m, H1, H3, H4, H5, H7, H11, H12), 3.63 (q, J = 6.2 Hz, CH(CH$_3$)Ph), 4.90 (d, J = 7.7 Hz, H10), 7.00–7.35 (m, 5 × CH(Ph)). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 22.21 (C9), 23.72 (C13), 25.07 (CH(CH$_3$)Ph), 25.98 (C8), 30.05 (C4), 36.91 (C7), 39.69 (C6), 42.10, 47.77, 50.95, 54.33, 54.83, 58.70 (C1, C3, C5, C11, C12, CH(CH$_3$)Ph), 81.08 (C10), 126.30, 126.52 (CH(Ph)), 126.74 (C2), 128.22 (CH(Ph)), 146.40 (C(Ph)), 212.05 (CO). IR (hexane): ν(C≡O) = 2038, 1974, 1962 cm^{-1}. Anal. Found: C, 66.86; H, 7.46; N, 3.01. $C_{24}H_{29}FeNO_3$ (435.34). Calc.: C, 66.21; H, 6.71; N, 3.21%. EI–MS (m/z (rel. int.)): M$^+$-CO 407 (0.2), M$^+$-2CO 379 (5.2), M$^+$-3CO 351 (80.4), M$^+$-Fe(CO)$_3$ 295 (14.2), $C_8H_{12}N$ 122 (17.2), C_8H_9 105.0 (100).

3.1.10. Tricarbonyl[η^4-4-[(1R)-6,6-dimethyl-bicyclo-[3.1.1]-hept-2-en-2-yl]-(Z)-(2S)-2-N-(1R)-(1-phenyleth-ylamino)-but-3-ene]iron (14A)

Method (c); eluent, hexane/ether (10:1 to 3:1), yellow-orange oil, yield 0.39 g (54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 1.02 (s, 3H, H9), 1.16 (d, J = 5.4 Hz, 3H, H13), 1.24 (d, J = 6.7 Hz, 3H, CH(CH_3)Ph), 1.42 (s, H8, obscures particularly the d of H7), 1.80–2.20, 2.35–2.45, 2.52–2.66 (3m, H1, H3, H4, H5, H7, H12), 3.74 (q, J = 6.5 Hz, CH(CH$_3$)Ph), 5.14 (d, J = 6.7 Hz, H10), 7.12–7.32 (m, 5H, 5 × CH(Ph)). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) = 22.15, 22.42 (C9, C13), 23.99 (CH(CH$_3$)Ph)), 25.96 (C8), 29.94 (C4), 36.99 (C7), 39.55 (C6), 42.05, 47.81, 49.44, 54.38, 54.55, 58.67 (C1, C3, C5, C11, C12, CH(CH$_3$)Ph), 81.18 (C10), 126.30 (CH(Ph)), 126.78 (C2), 126.86, 128.34 (CH(Ph)), 145.06 (C(Ph)), 211.90 (CO). IR (hexane): ν(C≡O) = 2038, 1974, 1962 cm^{-1}. Anal. Found: C, 66.82; H, 7.69; N, 3.20. $C_{24}H_{29}FeNO_3$ (435.34). Calc.: C, 66.21; H, 6.71; N, 3.21%. EI–MS (m/z (rel. int.)): M$^+$-CO 407 (0.3), M$^+$-2CO 379 (6.8), M$^+$-3CO 351 (52.8), M$^+$-Fe(CO)$_3$ 295 (11.4), $C_8H_{12}N$ 122 (13.8), C_8H_9 105.0 (100).

3.3. Kinetic resolution of (R/S)-phenylethylamine by reaction with 4 at −78°C

(R/S)-Phenylethylamine (0.50 g, 4.13 mmol, 0.53 ml, 2.2 eq) was dissolved in methylene chloride (50.0 ml) and the solution was cooled to −78°C. A solution of the optically active cation **4** (0.76 g, 1.88 mmol) in methylene chloride (20.0 ml) was added dropwise to the reaction mixture (0.5 h). After stirring for 2.5 h at −78°C, EtN(^{i}Pr)$_2$ (0.29 g, 2.26 mmol, 1.2 eq) was added and the reaction mixture slowly warmed to room temperature. The solvent was evaporated in vacuo and the residue was purified by chromatography (SiO_2; eluent, hexane/ether (10:1) to ether). Two fractions, (*E,Z*)-**13A** (0.12 g, 15%) and (*E,Z*)-**14A** (0.27 g, 33%),

were obtained as orange oils. The ^{13}C NMR spectra are in accordance with those of (*E,Z*)-**13A** and (*E,Z*)-**14A**.

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