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REACTIVITY OF π-PENTADIENYL COMPLEXES. STEREOCHEMISTRY OF THE ADDITION OF AMINES TO THE (*syn,syn*-1,5-DIMETHYLPENTADIENYL)IRON TRICARBONYL CATION

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SUMMARY

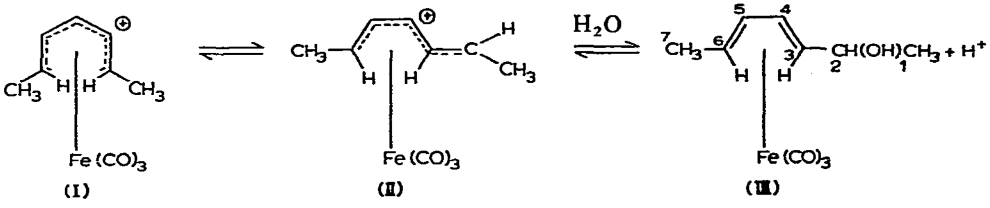
Strongly basic amines react with the (*syn,syn*-1,5-dimethylpentadienyl)iron tricarbonyl cation to give (*cis,trans*-dienylamine)iron tricarbonyl complexes through an *exo* attack of the nucleophile on the coordinated pentadienyl group. Weakly basic amines give (*trans,trans*-dienylamine)iron tricarbonyl complexes, *i.e.*, the reaction proceeds with geometrical inversion.

The stereochemistry of the new complexes has been elucidated by NMR, CD and X-ray analysis.

INTRODUCTION

The reaction of (*syn,syn*-1,5-dimethylpentadienyl)iron tricarbonyl cation (I) with water was shown by Mahler and Pettit[1] to proceed with geometrical inversion to give (*trans,trans*-hepta-3,5-dien-2-ol)iron tricarbonyl (III). The nucleophilic attack of water on cation (I) is stereospecific, since it gives only one of the two diastereoisomers differentiable for the configuration of the two independent chiral centres C-2 and C-3 of the dienol complex. According to the mechanism proposed by Mahler and Pettit, which involves an equilibrium between the *cis* (I) and the *trans* (II) (1,5-dimethylpentadienyl)iron tricarbonyl cation** and an *exo* attack of water on the last cation, the C-2 and C-3 carbon atoms have the same absolute configuration (Scheme 1).

SCHEME 1



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** The existence of an equilibrium between *cis*- and *trans*-pentadienyliron tricarbonyl cations has been recently demonstrated by low temperature NMR experiments[2].

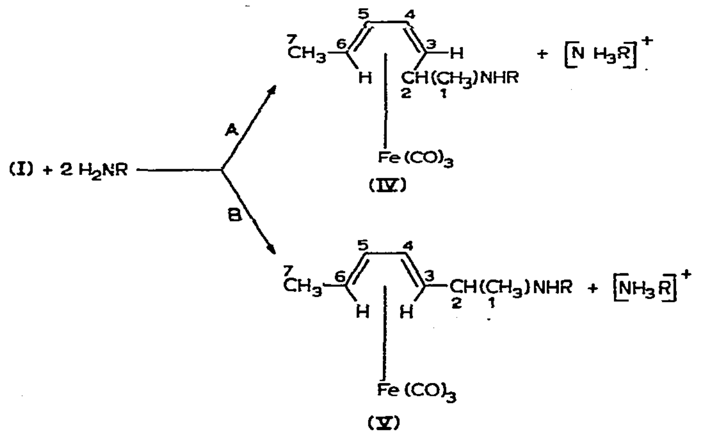
However, the reaction of pentadienyliron tricarbonyl cations with nucleophiles seems not always to be accompanied by geometrical inversion; thus, the reaction of salts of pentadienyliron tricarbonyl cation with sodium borohydride gives a mixture of 80% (*cis*-1,3-pentadiene) and 20% (*trans*-1,3-pentadiene)iron tricarbonyl complexes[1].

We consider below the stereochemistry of the addition of amines to (I). It will be shown that (2-amino-*trans,trans*-3,5-heptadiene)- or (2-amino-*cis,trans*-3,5-heptadiene)iron tricarbonyl complexes are obtained depending upon the base strength of the reaction conditions. Preliminary results were recently published[3].

RESULTS AND DISCUSSION

The reactions of amines with (*syn,syn*-1,5-dimethylpentadienyl)iron tricarbonyl cation (I) were carried out in a homogeneous phase. Methylene chloride solutions of the fluoroborate salt of (I) were added to the amine dissolved in the same solvent. The reaction pathway is illustrated in Scheme 2.

SCHEME 2



Strongly basic amines (pK_b 3–6)[4] such as isopropylamine, ethylamine, and methylbenzylamine react with (I) by route A of Scheme 2. Compounds of type (IV) are exclusively formed as shown by TLC examination of the reaction mixture. Arylamines (pK_b 10–13) such as *p*-bromoaniline, *m*-nitroaniline and *p*-nitroaniline give quantitative yields of compounds of type (V). In both cases the concentration of the amine is not decisive for the steric course of the reaction; however aniline (pK_b 9.4) and *p*-toluidine (pK_b 8.9) showed to have an intermediate behaviour. Thus *p*-toluidine reacts according either to route A or route B if stoichiometric amounts of the amine are brought into reaction with (I) in concentrated or diluted solutions respectively. Aniline follows route B if stoichiometric amounts of the amine are used with (I), but route A is followed if a large excess of the amine is used.

It is noteworthy that even *p*-bromoaniline (pK_b 10.1) gives small amounts of the (*cis,trans*-dienylamine)iron tricarbonyl complex in addition to the expected *trans,trans* complex when the solid fluoroborate salt of cation (I) is added to the molten amine.

TABLE 1

NMR DATA FOR (*cis*, *trans*-DIENYLAMINE)IRON TRICARBONYL COMPLEXES[a]

R	Chemical shifts, τ						
	H-4	H-5	H-3	H-6	H-2	CH_3-1	CH_3-7
$CH(CH_3)_2$ Hydrochloride	4.59	4.59	7.78	7.48	~7.3	~8.6	~8.6
$CH_2C_6H_5$[b] Hydrochloride	4.52	4.52	~7.7	~7.7	7.23	8.51	8.57
$CH(CH_3)C_6H_5$ Hydrochloride (−) diastereoisomer	~4.7	~4.7	~7.7	8.33	~7.7	8.62	8.72
$CH(CH_3)C_6H_5$ Hydrochloride (+)diastereoisomer	~4.5	~4.5	~7.6	~8.3	~7.6	8.48	8.73
$C_6H_4CH_3$-*p*	5.35	5.10	~7.9	~7.9	7.30	8.88	8.78
C_6H_5[c]	5.20	4.87	~7.8	~7.6	7.06	~8.7	~8.6
C_6H_4Br-*p*	5.12	4.80	7.87	7.65	7.12	8.70	8.55
$C_{10}H_{11}FeO_3$[d] Hydrochloride diastereoisomer 1°	4.83	4.56	7.93	7.61	7.30	8.62	8.50
$C_{10}H_{11}FeO_3$[d] Hydrochloride diastereoisomer 2°	4.78	4.50	7.90	7.62	~7.4	8.72	8.51

[a] TMS as internal standard. The solvent was methanol-d_4, except for the *p*-toluidine and *p*-bromoaniline derivatives for which chloroform-*d* was used. [b] The methylenic protons of the $CH_2C_6H_5$ group give rise to an AB spectrum centered at 5.97 τ, J_{AB} 12 Hz. [c] First order splittings: $J_{1,2}$ 6, $J_{2,3}$ 10, $J_{3,4}$ 8, $J_{4,5}$ 5, $J_{5,6}$ 10, $J_{6,7}$ 6 Hz; comparable values were found for all the other complexes. [d] These complexes are the diastereoisomers denoted by formula (VII) in the text.

(2-*Amino-cis,trans*-3,5-*heptadiene*)*iron tricarbonyl*

Table 1 lists the NMR data for the complexes having a *cis,trans*-dienylamine coordinated to the $Fe(CO)_3$ group [compounds of type (IV)]. The chemical shift values 7.6–8.3 τ for both the H-3 and the H-6 protons are taken as indicating that the

TABLE 2

NMR DATA FOR (*trans*, *trans*-DIENYLAMINE)IRON TRICARBONYL COMPLEXES[a]

R	Chemical shifts, τ							Solvent
	H-4	H-5	H-3	H-6	H-2	CH_3-7	CH_3-1	
$C_6H_4CH_3$	5.14	5.40	9.40	~9.1	6.85	8.78	8.78	Chloroform-*d*/ benzene-d_6(1/1)
C_6H_5 Fluoroborate	~4.9	~5.2	~9.2	~8.6	6.70	8.60	8.50	Methanol-d_4
C_6H_4Br-*p*[b]	4.88	5.06	9.20	8.85	6.79	8.62	8.70	Chloroform-*d*
$C_6H_4NO_2$-*p*	5.14	5.30	9.40	9.00	6.86	8.75	8.85	Chloroform-*d*
$C_6H_4NO_2$-*m*	4.83	5.02	9.18	8.80	6.70	8.60	8.66	Chloroform-*d*

[a] TMS as internal standard. [b] First order splittings: $J_{1,2}$ 6–7, $J_{2,3} \simeq J_{3,4}$ 9, $J_{4,5}$ 5, $J_{5,6}$ 8–9 Hz. Comparable values were found for the other complexes.

attack of the amines has occurred without geometrical inversion. However, by analogy with the NMR data reported by Pettit *et al.*[5] for *cis,trans*-diene complexes such as (*cis,trans*-2,4-hexadiene)iron tricarbonyl and for the (*cis*-1,3-pentadiene)iron tricarbonyl, the *syn* H-3 proton should have a lower chemical shift (7.3–7.6 τ) than the *anti* H-6 proton (~8.6 τ). On the contrary, the chemical shift values found for the *anti* H-3 and H-6 protons of (*trans,trans*-dienylamine)iron tricarbonyls (Table 2) are comparable with those reported in literature for (*trans,trans*-diene)iron tricarbonyl complexes[5]. The NMR spectra of {2-[(*p*-bromophenyl)amino]-*cis,trans*-3,5-heptadiene}- and {2-[(*p*-bromophenyl)amino]-*trans,trans*-3,5-heptadiene}iron tricarbonyl as typical examples are shown in Fig. 1 and Fig. 2 respectively.

Presumably the shift at higher field of the *syn* H-3 proton and that at lower field of the *anti* H-6 proton of the (*cis,trans*-dienylamine)iron tricarbonyl complexes, with respect to the values reported by Pettit for the above mentioned *cis,trans* and *cis* diene complexes, are due to a different shielding effect of the iron in the two types of compounds. Interestingly, the X-ray structural determination of [2-(phenylamino)-*cis,trans*-3,5-heptadiene]iron tricarbonyl, which is now being refined at our laboratories[6], has shown that the C-3, C-2 bond deviates by 60° from the plane of the diene away from the iron, the distance between C-2 and H-6 being 2.6 Å. These preliminary crystallographic results indicate a deviation of the C-3 carbon atom from trigonal to tetragonal hybridization in order to relieve the steric interaction between the anti bulky group attached to the C-3 carbon atom and the H-6 proton*.

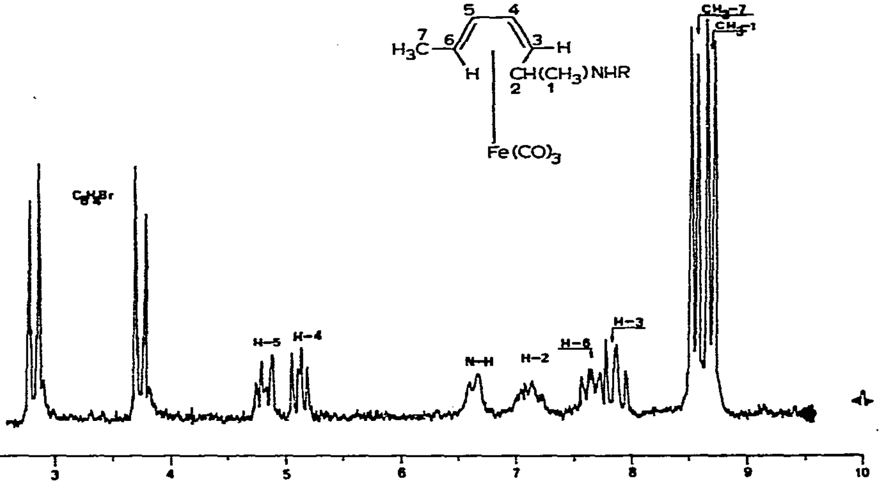


Fig. 1. NMR spectrum of {2-[(*p*-bromophenyl)amino]-*cis,trans*-3,5-heptadiene}iron tricarbonyl in chloroform-*d*.

The CD spectra of the two diastereoisomers obtained when (I) is caused to react with *S*-(α-methylbenzyl)amine are particularly revealing for a further elucidation of the stereochemistry of complexes (IV).

The reaction of (I) with an asymmetric amine affords two diastereoisomers,

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* In (*trans,trans*-2,4-hexadienoic acid)iron tricarbonyl where there is no such steric strain, Eiss[7] has found that all the carbon atoms of the diene moiety have essentially sp^2 hybridization.

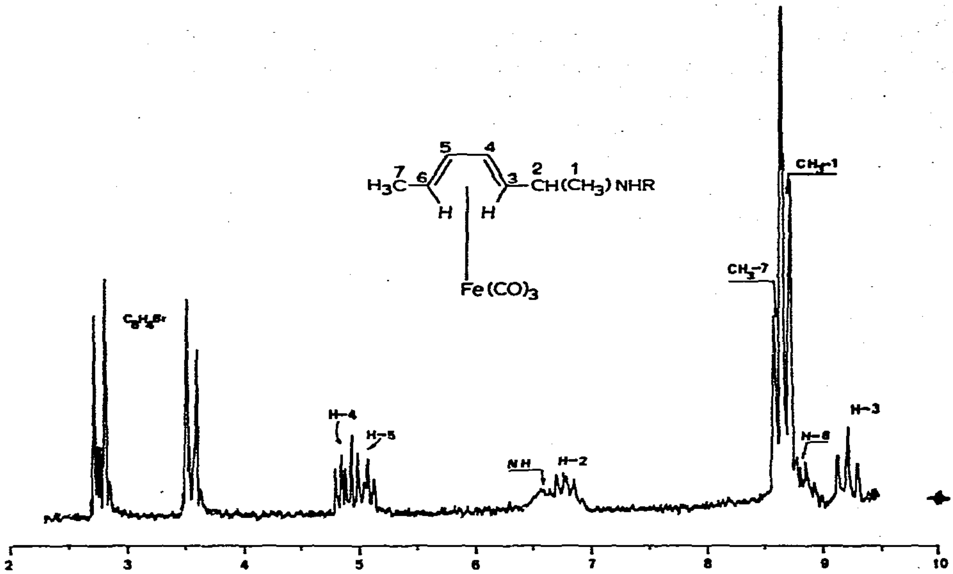


Fig. 2. NMR spectrum of {2-[(*p*-bromophenyl)amino]-*trans,trans*-3,5-heptadiene}iron tricarbonyl in chloroform-*d*.

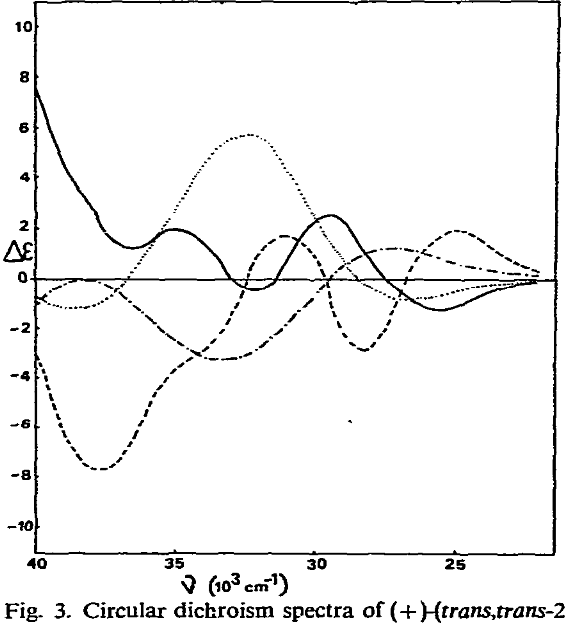
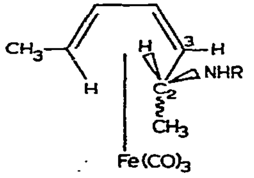


Fig. 3. Circular dichroism spectra of (+)-(*trans,trans*-2,4-hexadienoic acid)iron tricarbonyl (——), (−)-(*trans,trans*-2,4-hexadienal)iron tricarbonyl (– – – –), (+)-{2-[*S*-(α-methylbenzyl)amino]-*cis,trans*-3,5-heptadiene}iron tricarbonyl (–·–·–), (—)-{2[*S*-(α-methylbenzyl)amino]-*cis,trans*-3,5-heptadiene}iron tricarbonyl (·····) in methanol solutions.

since the nucleophilic attack may occur on either terminal carbon atoms of the coordinated pentadienyl group, which have opposite configuration. The CD spectra of the two diastereoisomers (Fig. 3) have the same pattern, but are opposite in sign, which indicates that the two diastereoisomers differ in the absolute configuration of the carbon atoms of the diene group. Moreover, the spectra are significantly different from those of optically-active (*trans,trans*-diene)iron tricarbonyl complexes. The most significant difference is in the low energy region, which should reflect the absolute configuration of the coordinated ligand[10]. The CD spectra of (+)-(*trans,trans*-2,4-hexadienoic acid)iron tricarbonyl and (−)-(*trans,trans*-2,4-hexadienal)iron tricarbonyl[8,9] are shown for comparison in Fig. 3. In the (*trans,trans*-diene)iron tricarbonyl complexes the terminal carbon atoms of the diene ligand have opposite configurations, whereas in the (*cis,trans*-dienylamine)iron tricarbonyl complexes they have the same configuration irrespective of whether there is *exo* or *endo* attack by the amine. Accordingly, the CD spectra of the (*trans,trans*-diene)iron tricarbonyl complexes have two maxima of opposite sign at 390 and 345 nm, whereas the spectra of (*cis,trans*-dienylamine)iron tricarbonyl complexes display only one maximum in the same region (370 nm). These low energies transitions may be assigned to *d–d* transitions of the iron.

It is noteworthy that the carbon atom C-2 of compounds (IV) is chiral, but following the arguments by Pino *et al.*[11] for olefin–platinum complexes, we believe that the sign of the low energy *d–d* transition of the iron reflects only the absolute configuration of the trigonal carbon atoms of the coordinated diene, the contribution of a possible asymmetric tetragonal carbon atom in α position with respect to the coordinated double bond being neglegible.

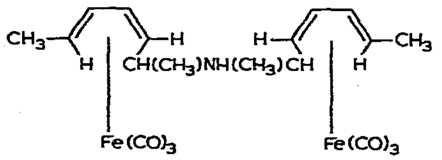
The *exo* attack of the nucleophile on the coordinated pentadienyl group, which is sterically more favorable than *endo* attack because of the bulkiness of the $Fe(CO)_3$ group, has been unambiguously demonstrated by a preliminary X-ray structure determination of the hydrochloride of (−)-{2-[*S*-(α-methylbenzyl)amino]-*cis,trans*-3,5-heptadiene}iron tricarbonyl[3]. The *R,R* configuration of the C-2 and C-3 carbon atoms is consistent only with an *exo* attack of the nucleophile on (I) [formula (VI)].



$R = S\text{-}CH(CH_3)C_6H_5$

(VI)

Finally, gaseous ammonia reacts with methylene chloride solutions of (I) by route A of Scheme 2, but the reaction proceeds further to give complexes of type (VII).



(VII)

If *exo* attack of the nucleophile is still operative, since the two coordinated diene moieties may have the same or opposite configuration two diastereoisomers of type (VII) are possible, one of which is a racemate and the other a *meso* form. The two expected diastereoisomers have been isolated by column chromatography. Structure (VII) has been confirmed for both complexes by elemental analyses and NMR spectra (Table 1).

(2-*Amino-trans,trans*-3,5-*heptadiene*)*iron tricarbonyl*

The NMR data of the complexes are summarized in Table 2. A typical NMR spectrum is shown in Fig. 2. The chemical shift values of the H-3 and H-6 protons are consistent with *trans,trans* coordination of the diene. We suppose that the reaction mechanism proposed by Pettit for the reaction of (I) with water (Scheme 1) applies also in this case, so that carbon atoms C-2 and C-3 (V) have the same absolute configuration.

CONCLUSIONS

The reaction of (*syn,syn*-1,5-dimethylpentadienyl)iron tricarbonyl cation (I) with amines can take place by two different stereochemical pathways. Alkylamines (pK_b 3–6) afford stereospecifically *cis,trans*-diene complexes of type (IV). The *exo* attack of the nucleophile on (I), as unambiguously proved by the X-ray structural determination[3] of (−)-{2-[*S*-(α-methylbenzyl)ammonium]-*cis,trans*-3,5-heptadiene}-iron tricarbonyl chloride, results in the same configuration for the two independent chiral centres C-2 and C-3.

If arylamines (pK_b 10) are allowed to react with (I), *trans,trans*-dienylamine complexes of type (V) are obtained. The reaction mechanism is probably analogous to that described by Mahler and Pettit[1] for the reaction of the same cation with water (Scheme 1).

By assuming that (*cis,trans*-dienylamine)iron tricarbonyl complexes are thermodynamically less stable than (*trans,trans*-dienylamine)iron tricarbonyl complexes owing to the steric interaction of the $-CH(CH_3)NHR$ group with the H-6 proton, it may be concluded that strongly basic amines give products determined by kinetic control whereas weakly basic amines give products determined by thermodynamic control. *p*-Toluidine (pK_b 8.9) shows an intermediate behaviour: the (*trans,trans*-dienylamine)- or (*cis,trans*-dienylamine)iron tricarbonyl complex may be prepared by changing the concentrations of the reacting amine.

EXPERIMENTAL

NMR spectra were run on a Varian Associates HA-100 spectrometer. CD spectra were obtained on a Jouan-Roussel CD 185 dichrograph. Melting points are uncorrected. Elemental analyses were performed by the A. Bernhardt Mikroanalytisches Laboratorium, Elbach, W. Germany. Anhydrous solvents were used. (*syn,syn*-1,5-Dimethylpentadienyl)iron tricarbonyl fluoroborate was prepared by the procedure described by Mahler and Pettit[1].

The (*cis,trans*-dienylamine)- and (*trans,trans*-dienylamine)iron tricarbonyl complexes prepared are listed in Table 3, along with the elemental analyses and melting points. In cases in which the dienylamine complexes were oils at room temperature, the elemental analyses and the NMR spectra were performed on the corresponding hydrochloride of fluoroborate salts, which can be easily crystallized, in order to

TABLE 3

ANALYTICAL DATA [a,b]

Compound		Analysis found (calcd.) (%)			M.p.
Nu.	R	C	H	N	(°C)
(IVa)	$CH(CH_3)_2$	41.44	5.75	3.71	118
	Fluoroborate	(41.01)	(5.25)	(3.68)	
(IVb)	$CH_2C_6H_5$	47.62	4.69	3.10	174 (dec.)
	Fluoroborate	(47.62)	(4.66)	(3.26)	
(IVc)	$CH(CH_3)C_6H_5$	49.37	5.16	3.22	110
	Fluoroborate	(48.82)	(4.97)	(3.16)	
	(+)diastereoisomer				
(IVd)	$CH(CH_3)C_6H_5$	55.11	5.66	3.61	128 (dec.)
	Hydrochloride,	(55.19)	(5.62)	(3.87)	
	(−) diastereoisomer				
(IVe)	$C_6H_4CH_3$-*p*	n.d.[c]	n.d.[c]	n.d.[c]	
(IVf)	C_6H_5	58.39	5.16	3.89	81
		(58.77)	(5.20)	(4.28)	
(IVg)	C_6H_4Br-*p*	47.22	3.97	3.49	66
		(47.34)	(3.94)	(3.46)	
(IVh)	$C_{10}H_{11}FeO_3$[d,e]	49.89	5.03	2.90	117
	Diastereoisomer 1°	(49.54)	(4.74)	(2.89)	
(IVi)	$C_{10}H_{11}FeO_3$[d,e]	49.95	4.75	2.77	85–86
	Diastereoisomer 2°	(49.54)	(4.74)	(2.89)	
(Va)	$C_6H_4CH_3$-*p*	58.63	5.44	3.83	75
		(59.88)	(5.57)	(4.10)	
(Vb)	C_6H_5	46.51	4.31	3.24	122–123
	Fluoroborate	(45.99)	(4.34)	(3.37)	
(Vc)	C_6H_4Br-*p*	47.56	4.23	3.35	121–122
		(47.34)	(4.21)	(3.46)	
(Vd)	$C_6H_4NO_2$-*m*	51.62	4.38	7.40	95 (dec.)
		(51.66)	(4.30)	(7.55)	
(Ve)	$C_6H_4NO_2$-*p*	51.62	4.41	7.34	75
		(51.66)	(4.30)	(7.55)	

[a] The IR spectra (hexane) of the (dienylamine)iron tricarbonyl complexes showed three $\nu(C{\equiv}O)$ bands at 2049–2052, 1980–1984, 1974–1978 cm^{-1}. [b] The complexes are yellow or orange yellow, the corresponding salts (hydrochloride or fluoroborate) pale yellow. [c] The compound is an oil at room temperature. The corresponding hydrochloride or fluoroborate salt could not be isolated. [d] These complexes have the formula (VII) in the text. [e] Calcd. for R=H: C, 47.81; H, 5.18; N, 5.58%.

ensure the analytical purity of the samples.

Compounds (IVa), (IVb), (IVe), (Vb)–(Ve) of Table 3 were prepared with the following procedure: methylene chloride solutions of the pentadienyl cation were added to stoichiometric amounts of the amine (molar ratio 1/2) dissolved in the same solvent. The reaction mixture was stirred for 30 min. The residue obtained upon evaporation of the solvent was extracted with ether and chromatographed on a silica gel column. Ether was generally used as the eluent. When oily compounds were obtained, they were readily converted into the solid hydrochloride or fluoroborate salts by adding the acid to ethanol solutions of the oils. Acid addition was stopped at pH 5. Well shaped pale yellow crystals were obtained by adding ether to the alcoholic solutions. The fluoroborate salts may be directly obtained by treating the pentadienyl cation with the amines in a 1/1 molar ratio.

(+)- and (−)-{2-[S-(α-methylbenzyl)amino]-cis,trans-3,5-heptadiene}iron tricarbonyl

A solution of (*syn,syn*-1,5-dimethylpentadienyl)iron tricarbonyl fluoroborate [0.45 g (1.4 mmoles)] in methylene chloride (15 ml) was added slowly to 0.35 g (2.9 mmoles) of *S*-(α-methylbenzyl)amine [$[\alpha]_{589}$ −39.2] in 10 ml of methylene chloride. The mixture was stirred for 30 min, then the solvent was evaporated at reduced pressure. The residue was extracted several times with ether. The ethereal extracts were concentrated and chromatographed on silica gel column with ether as eluent. Two yellow bands developed. The fraction corresponding to the first band had a positive optical activity, while that corresponding to the second band had a negative value. Each fraction was repeatedly chromatographed and finally upon evaporation of the solvent two oily products were obtained having $[\alpha]_{589}$ +240 (*c* 0.4, methanol) (fraction 1) and $[\alpha]_{589}$ −203 (*c* 0.4, methanol) (fraction 2). The two products were shown to be pure by silica gel TLC examination.

Reaction of (syn,syn-1,5-dimethylpentadienyl)iron tricarbonyl fluoroborate with ammonia

The salt (1.0 g) was dissolved in 15 ml of methylene chloride. Ammonia was bubbled through the solution for 15 min. The solvent was evaporated off, the residue was extracted with ether and chromatographed on silica gel column with ether as eluent. Three fractions were isolated. The first fraction (0.2 g) even after several chromatographic treatments did not yield pure samples (TLC test) and was not further investigated. The second and third fractions each yielded 0.3 g of yellow compounds which are the diastereoisomeric complexes indicated in Tables 1 and 3 as diastereoisomers 1° and 2° respectively. Analytical pure samples were obtained by crystallization from pentane/ether mixture (5/1).

{2-[(p-Methylphenyl)amino]-trans,trans-3,5-heptadiene}iron tricarbonyl

(*syn,syn*-1,5-Dimethylpentadienyl)iron tricarbonyl fluoroborate [0.32 g (1.0 mmoles)] was dissolved in 250 ml of methylene chloride, and 0.21 g (2.0 mmoles) of *p*-toluidine in 50 ml of methylene chloride was added dropwise at 0° with stirring. After a further 10 min of stirring, the solvent was evaporated off, and the residue was extracted with ether and chromatographed on silica gel column with ether as eluent to yield 0.29 g of yellow crystals.

[2-(Phenylamino)-cis,trans-3,5-heptadiene]iron tricarbonyl

Aniline [2.10 g (22.6 mmoles)] dissolved in 5 ml of methylene chloride was added dropwise to 0.32 g (1.0 mmole) of (*syn,syn*-1,5-dimethylpentadienyl)iron tricarbonyl fluoroborate in 4.5 ml of methylene chloride. After a few minutes stirring, the solvent was evaporated off and the oily residue was purified by chromatography on silica gel with ether/hexane (1/1) as the eluent. Yellow crystals (0.35 g) were obtained.

[2-(p-Bromoaniline)-cis,trans-3,5-heptadiene]iron tricarbonyl

(*syn,syn*-1,5-Dimethylpentadienyl)iron tricarbonyl fluoroborate [0.64 g (2 mmoles)] was added with stirring to 5.6 g (25 mmoles) of molten *p*-bromoaniline (at 70°). After cooling to room temperature the yellow mixture was dissolved in ether and chromatographed to give a semisolid product which was shown by NMR analysis to be a 3/1 mixture of the (*trans,trans*-dienylamine)- and (*cis,trans*-dienylamine)iron tricarbonyl complexes.

The pure complexes were obtained by fractional crystallization of the crude mixture from ether/hexane (1/2). The *trans,trans* complex separated first.

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REFERENCES

1 J. E. MAHLER AND R. PETTIT, *J. Amer. Chem. Soc.*, 85 (1963) 3955.
2 T. S. SORENSEN AND C. R. JABLONSKI, *J. Organometal. Chem.*, 25 (1970) C 62; C. P. LILLYA AND R. A. SAHATJIAN, *J. Organometal. Chem.*, 25 (1970) C 67.
3 G. MAGLIO, A. MUSCO, R. PALUMBO AND A. SIRIGU, *Chem. Commun.*, (1971) 100.
4 R. C. WEAST, *Handbook of Chemistry and Physics*, The Chemical Rubber Co., Cleveland Ohio (1969–1970), pp. D115–D117.
5 G. F. EMERSON, J. E. MAHLER, R. KOCHHAR AND R. PETTIT, *J. Org. Chem.*, 29 (1964) 3620.
6 A. IMMIRZI, private communication.
7 R. EISS, *Inorg. Chem.*, 9 (1970) 1650.
8 A. MUSCO, G. PAIARO AND R. PALUMBO, *Ric. Scient.*, 39 (1969) 417.
9 A. MUSCO, R. PALUMBO AND G. PAIARO, *Inorg. Chim. Acta*, in the press.
10 P. CORRADINI, S. F. MASON, G. PAIARO, A. PANUNZI AND G. M. SEARLE, *J. Amer. Chem. Soc.*, 88 (1966) 2863; A. D. WRIXON, E. PREMUZIC AND A. SCOTT, *Chem. Commun.*, (1968) 639.
11 R. LAZZARONI, P. SALVADORI AND P. PINO, *Chem. Commun.*, (1970) 1164.