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THE STEREOSPECIFICITY AT THE IRON CENTER OF THE DECARBONYLATION OF AN IRON—ACETYL COMPLEX

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Summary

The dinuclear complex $[(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$ was synthesized by reaction of $Fe_2(CO)_9$ with 1-methyl-3-phenylcyclopentadiene; it was converted to $(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2CH_3$ by reduction with sodium amalgam and addition of CH_3I, and thence to $(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3](COCH_3)$ (I) by reaction with $P(C_6H_5)_3$. The acetyl I was separated into two diastereomerically related pairs of enantiomers, Ia and Ib, by a combination of column chromatography on alumina and crystallization from benzene/pentane. The photochemical decarbonylation of Ia and Ib in benzene or THF solution was examined by ^1H NMR spectroscopy. This reaction proceeds with high stereospecificity (> 84% retention or inversion) at the iron center to yield $(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$(II), enriched in the diastereomerically related pairs of enantiomers, IIa and IIb, respectively. Since IIa and IIb epimerize under the photolytic conditions of decarbonylation, the actual stereospecificity of the conversion of I to II is higher than 84%, and likely 100%. This is supported by the data from kinetic studies of the decarbonylation of I and the epimerization of II, carried out under identical photolytic conditions. The implications of the foregoing results to the mechanism of the decarbonylation are considered. Also described herein is the synthesis of other complexes with two asymmetric centers of the general formula (h^5-cyclopentadienyl)Fe(CO)(L)(COR) and (h^5-cyclopentadienyl)Fe(CO)(L)R that contain either an unsymmetrically substituted h^5-cyclopentadienyl ring or a chiral tertiary phosphine.

Introduction

In recent years the study of insertion and elimination reactions in organometallic chemistry has evolved largely as a result of the demonstrated importance of these processes in numerous catalytic systems, e.g. the Oxo reaction, the polymerization of olefins and catalytic hydrogenation. Some of the most widely investigated insertion reactions have been the carbonylation and the decarbonylation of transition metal—alkyl and —acyl complexes, respectively [1].

Studies have been conducted of the mechanism of the CO insertion reaction of several types of transition metal—alkyl complexes with nucleophiles such as CO, tertiary phosphines, phosphites and amines [2-10]. The stereochemistry of CO insertion and decarbonylation has also been extensively investigated. The decarbonylation of *cis*-$(CH_3CO)Mn(^{13}CO)(CO)_4$ was shown to proceed by a "methyl migration" mechanism [11]. A retention of configuration at the α carbon of the alkyl moiety has been observed both in the carbonylation of *erythro*-h^5-$C_5H_5Fe(CO)_2CHDCHDC(CH_3)_3$ with $P(C_6H_5)_3$ and in the photochemical decarbonylation of *erythro*-h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3][COCHDCHDC(CH_3)_3]$ [12]. In order to furnish stereochemical information about the metal center and to complement the aforementioned kinetic and stereochemical investigations, we have examined the stereochemistry at the iron atom of the photochemical decarbonylation of a pseudotetrahedral, chiral iron complex.

Complexes of the general formula (h^5-cyclopentadienyl)Fe(CO)(L)R, where R = alkyl or acyl, provide useful models for studies of the stereochemistry of the metal during reaction at the Fe—R bond. The iron atom is situated in an asymmetric, pseudotetrahedral environment. ^1H NMR studies have shown that the methylene protons of the benzyl group in h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]$-$(COCH_2C_6H_5)$ [13] and h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ [14], as well as the *gem*-methyl groups in h^5-$C_5H_5Fe(CO)[P(CH_3)_2C_6H_5](COCH_3)$ [13], are magnetically nonequivalent. The observed magnetic nonequivalence of these groups confirms the presence of an asymmetric metal atom and demonstrates a high degree of configurational stability at the iron center. Consistent with the above, the synthesis and separation into optical isomers of a number of asymmetric, pseudotetrahedral transition metal complexes have been recently reported [15-17].

In a previous paper from this laboratory a study has been reported on the stereochemistry at the iron center of the decarbonylation of h^5-$C_5H_5Fe(CO)$-$[P(C_6H_5)_3][COCH_2CH(CH_3)C_6H_5]$ [18]. However, the resulting alkyl complex, h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3]CH_2CH(CH_3)C_6H_5$, showed only moderate configurational stability, thus precluding a precise determination of the stereospecificity of this reaction. In order possibly to circumvent this difficulty we have now designed and synthesized chiral iron—acyl and —alkyl complexes of the general formula (h^5-cyclopentadienyl)$Fe(CO)[P(C_6H_5)_3]R$ which contain an unsymmetrically substituted *pentahapto*-cyclopentadienyl ring as well as an asymmetric metal. The compounds $(h^5$-1-CH_3-3-$C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3][COCH_3]$ (I) and $(h^5$-1-CH_3-3-$C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (II) were separated into two diastereomerically related pairs of enantiomers, (*RR*), (*SS*) and (*RS*), (*SR*). The stereospecificity at the iron during the photochemical decarbonylation of I to II was studied by ^1H NMR spectroscopy. Part of this work has been described in a preliminary communication [19].

Experimental

All organometallic reactions were conducted under an atmosphere of nitrogen. Neutral alumina (Ventron) used for chromatography and filtration was deactivated with distilled water (5%).

Iron pentacarbonyl was purchased from Alfa Inorganics. Diiron nonacarbonyl was prepared according to King [20]. Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under a nitrogen atmosphere. Reagent grade benzene and technical grade pentane were distilled from CaH_2, piperidine from NaOH, and acetonitrile from P_4O_{10}. Indene and $C_6H_5CH_2COCH_3$ were also purified by distillation prior to use. *p*-Toluenesulfonyl chloride was recrystallized from ethanol. All other procured chemicals and solvents were reagent grade and were used as received.

3-Phenyl-2-cyclopentenone [21], 2,3,4-triphenyl-2-cyclopentenone [22], 1-indanone [23], and $C_6H_5COCH_2Br$ [24] were prepared as described in the literature. 1-Methyl-3-phenylcyclopentadiene [25], 2-methyl-3,4,5-triphenylcyclopentadiene [26], and 3-methylindene [27] were obtained by treatment of 3-phenyl-2-cyclopentenone, 2,3,4-triphenyl-2-cyclopentenone, and 1-indanone, respectively, with CH_3MgI. *p*-Toluenesulfonyl azide was prepared from *p*-toluenesulfonyl chloride and NaN_3 in THF [28]. The alkyl h^5-$C_5H_5Fe(CO)_2CH_3$ was obtained by the reaction of $Na[h^5\text{-}C_5H_5Fe(CO)_2]$ with CH_3I [29]. Methyl-β-naphthylphenylphosphine was synthesized by the action of Si_2Cl_6 on methyl-β-naphthylphenylphosphine oxide [30], employing the procedure of Mislow [31]. *S*-(+)-(2-Phenylbutyl)diphenylphosphine was a gift from Professor J.D. Morrison.

1-Diazo-2-methyl-3,4,5-triphenylcyclopentadiene was prepared from *p*-toluenesulfonyl azide and 2-methyl-3,4,5-triphenylcyclopentadiene in the presence of piperidine in acetonitrile at room temperature in a manner analogous to that reported for diazotriphenylcyclopentadiene and diazotetraphenylcyclopentadiene [32]. After chromatography on alumina, the solvent was removed and the product was crystallized from ether/pentane to afford orange crystals (48% yield) of 1-diazo-2-methyl-3,4,5-triphenylcyclopentadiene, m.p. 192°, $\nu(NN)$ 2063 cm^{-1}, ^1H NMR ($CDCl_3$) τ 7.79s (3H), 2.5-2.9m (15H).

Infrared spectra were recorded either on a Perkin—Elmer Model 337 spectrophotometer or on a Beckman Model IR-9 spectrophotometer. ^1H NMR spectra were obtained on a JEOL JNM-MH-100 or a Varian A-60A spectrometer. Irradiation experiments were carried out in Pyrex tubes under nitrogen using a Rayonet Model RPR-100 photochemical reactor with 3500 Å lamps. Melting points were measured in vacuo with a Thomas—Hoover capillary melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Preparation of $[(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$

A suspension of 16 g (0.10 mol) of 1-methyl-3-phenylcyclopentadiene and 36 g (0.10 mol) of $Fe_2(CO)_9$ in 150 ml of benzene was stirred at room temperature for 21 h. The mixture was filtered, the volume of the filtrate was reduced, and the resulting concentrated solution was chromatographed on alumina. Elution with pentane afforded a yellow band which contained some unreacted 1-methyl-3-phenylcyclopentadiene. Then elution with benzene afforded a brown band which contained the product. After removal of the solvent and addition of pentane, 6.1 g (23% yield) of dark purple crystals of $[(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$ was obtained, $\nu(C{\equiv}O)$ 1987 vs, 1947 s cm^{-1}, $\nu(C{=}O)$ 1769 vs cm^{-1} (CH_2Cl_2 solution).

Preparation of (h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe$(CO)_2CH_3$

The salt Na[(h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe$(CO)_2$] was prepared by the reduction of 1.4 g (2.7 mmol) of [(h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe$(CO)_2]_2$ with 2% excess sodium amalgam in 50 ml of THF. To this solution was added 0.85 g (5.4 mmol) of CH_3I in 10 ml of THF. The resulting mixture was stirred for 3 h and then the solvent was removed. The residue was extracted with pentane and the extracts were filtered through 10 g of alumina. The pentane was removed at 20° to afford 1.2 g (79% yield) of the yellow crystals of (h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe$(CO)_2CH_3$ which melted upon warming to room temperature.

Preparation of (h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe(CO)[P$(C_6H_5)_3$]($COCH_3$) (I)

A solution of 1.2 g (4.2 mmol) of (h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe$(CO)_2CH_3$ and 1.1 g (4.2 mmol) of P$(C_6H_5)_3$ in 25 ml of CH_3CN was maintained at reflux for 16.5 h. The solvent was removed, and the residue was dissolved in a small amount of CH_2Cl_2 and chromatographed on alumina. Elution with pentane afforded some unreacted starting materials; elution with 3/1 CH_2Cl_2/benzene afforded a red band. The effluent was concentrated and pentane was added to yield 1.2 g (53%) of the orange crystals of I.

Preparation of (h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe(CO)[P$(C_6H_5)_3$]CH_3 (II)

A solution of 1.1 g (2.0 mmol) of I in 250 ml of benzene was irradiated for 3 h. It was then concentrated and chromatographed on alumina. Elution with 4/1 pentane/benzene afforded the red-colored product; elution with benzene gave the purple-colored cyclopentadienyliron dicarbonyl dimer; and elution with CH_2Cl_2 furnished the orange-colored starting material. Concentration of the effluents and addition of pentane afforded 0.79 g (75% yield) of II, 0.06 g (10% yield) of [(h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe$(CO)_2]_2$ and 0.10 g (8% recovery) of I.

Separation of the diastereomers of (h^5-1-CH_3-3-$C_6H_5C_5H_3$)Fe(CO)[P$(C_6H_5)_3$]($COCH_3$) (Ia and Ib)

Ia and Ib were separated by a combination of column chromatography and fractional crystallization. Approximately 1.5 g of a 50/50 mixture of Ia/Ib was dissolved in a minimum amount of benzene and chromatographed on a 2.7 × 37 cm column of alumina. With pentane as the eluent, I remained at the top of the column. As the eluent was changed from pentane to 2/1 pentane/benzene the large orange band moved slowly. This band was eluted and the solvent removed until 0.5 g of the solid had been collected. The remainder of the band was then eluted off with CH_2Cl_2, the solvent was removed and the residue was set aside.

The combined front fractions of separate chromatographies of three 1.5 g 50/50 mixtures of Ia/Ib were rechromatographed by the above procedure. The large orange band was divided into two portions. The front portion (0.75 g) was identified by NMR spectroscopy as a 95/5 mixture of Ia/Ib.

Approximately 2.6 g of a 35/65 mixture of Ia/Ib (obtained from the back fractions of the above-mentioned initial chromatographies) was dissolved in 50 ml of 4/1 pentane/benzene and was stored under nitrogen for 24 h at 5°. The crystals (1.7 g) were collected, washed with pentane, dissolved in 50 ml of 3/2

TABLE 1

ANALYTICAL DATA AND MELTING POINTS OF Ia/Ib AND IIa/IIb

Compound	M p. (°C)	Analysis found (calcd.) (%)	
		C	H
50/50 Ia/Ib	129-134 (dec.)	72.81 (72.81)	5.58 (5.37)
95/5 Ia/Ib	136-138 (dec.)	72.84 (72.81)	5.40 (5.37)
2/98 Ia/Ib	135-137 (dec.)	72.73 (72.81)	5.30 (5.37)
97/3 IIa/IIb	137-138 (dec.)	74.55 (74.43)	5.71 (5.66)
8/92 IIa/IIb	139-141 (dec.)	74.29 (74.43)	5.58 (5.66)

pentane/benzene and again stored for 24 h at 5°. The resulting crystals were filtered off and washed with pentane to yield 0.95 g of diastereomerically pure Ib as ascertained by NMR spectroscopy.

Analytical data and melting points of Ia/Ib are furnished in Table 1.

Separation of the diastereomers of $(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ *(IIa and IIb)*

A solution of 1.25 g of an 85/15 mixture of IIa/IIb (obtained from several successive photochemical decarbonylations of a 95/5 mixture of Ia/Ib for 15 min.) in 38 ml of 15/4 pentane/benzene was stored under nitrogen for 24 h at 5°. The resulting crystals were filtered off and washed with pentane to afford 0.715 g of a 97/3 mixture of IIa/IIb as identified by NMR spectroscopy.

A solution of 0.657 g of pure Ib in 250 ml of THF was irradiated for 5 min. Following usual work-up, 0.056 g of an 8/92 mixture of IIa/IIb was isolated. This procedure was repeated to accumulate larger amounts of an 8/92 mixture of IIa/IIb.

Analytical data and melting points of IIa/IIb are furnished in Table 1.

Photochemical decarbonylation of Ia and Ib

Benzene or THF solutions (ca. 4×10^{-3} to $7 \times 10^{-3} M$) of I enriched in Ia or Ib were irradiated for various periods of time under nitrogen. The solutions were then concentrated and chromatographed on an alumina column (2 × 20 cm). Elution with 4/1 pentane/benzene afforded II; elution with CH_2Cl_2 yielded unreacted I. The results of these experiments are given in Table 2.

TABLE 2

STEREOCHEMICAL RESULTS OF THE DECARBONYLATION OF Ia AND Ib

Solvent	Time (min.)	Starting Ia/Ib	Recovered Ia/Ib	Yield of II(%)	Product IIa/IIb	Stereo-specificity
Benzene (150 ml)	40	95/5 (0.504 g)	95/5 (0.180 g)	50	59/41 (0.241 g)	20
Benzene (250 ml)	15	95/5 (0.560 g)	95/5 (0.335 g)	28	84/16 (0.142 g)	76
Benzene (250 ml)	5	95/5 (1.010 g)	95/5 (0.910 g)	6	88/12 (0.055 g)	84
Benzene (250 ml)	5	0/100 (0.917 g)	0/100 (0.763 g)	6	8/92 (0.049 g)	84
THF (250 ml)	5	0/100 (0.755 g)	0/100 (0.657 g)	8	8/92 (0.059 g)	84

Configurational stability of IIa and IIb

An 84/16 mixture of IIa/IIb (0.144 g) was dissolved in a small volume of benzene and chromatographed on an alumina column (2 × 20 cm). Elution with 4/1 pentane/benzene afforded 0.141 g of an 83/17 mixture of IIa/IIb. Mixtures of IIa/IIb enriched in either IIa or IIb were found to be configurationally stable in benzene, THF, and CH_2Cl_2 for 4 h in the dark or in ordinary laboratory light under nitrogen at 25°. A solution of 0.060 g of an 85/15 mixture of IIa/IIb in $CDCl_3$ gradually epimerized with considerable decomposition over a 3 h period to a 60/40 mixture of IIa/IIb.

Kinetic investigation of the decarbonylation of a 95/5 mixture of Ia/Ib

Benzene solutions ($7.35 \times 10^{-3} M$) of a 95/5 mixture of Ia/Ib in 2.5 × 20 cm Pyrex tubes were irradiated for 10, 15, 20, and 25 min. The solutions were then concentrated and chromatographed on an alumina column (2.5 × 12 cm). Elution with 3/2 pentane/benzene afforded II; elution with CH_2Cl_2 yielded I. A trace of $[(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3Fe(CO)_2]_2$ was observed during chromatography of the 20 and 25 min. reaction mixtures. The results of these experiments are presented in Table 3 and in the Results and discussion section of this paper.

Photochemical epimerization of a 70/30 mixture of IIa/IIb

Benzene solutions ($2.28 \times 10^{-3} M$) of a 70/30 mixture of IIa/IIb were irradiated in Pyrex tubes (2.5 × 20 cm) for 5, 10, 15, and 20 min under nitrogen. After the solutions had been concentrated and filtered through one inch of alumina to remove the decomposition material, the solvent was evaporated. The results of these experiments are tabulated in the Results and discussion section of this paper.

Determination of the ratios of the diastereomers Ia/Ib and IIa/IIb

The ratios of the diastereomers of I were determined by multiple integration on the three diastereotopic (by external comparison) protons on the cyclopentadienyl ring between τ 5.20 and 6.38 on a JEOL JNM-MH-100 spectrometer. Generally, a base line could not be obtained between the signals for the two sets of diastereotopic (by external comparison) methyl groups. The ratios of the diastereomers of II were determined by peak height measurement of the methyl groups on the cyclopentadienyl ring. Peak height measurement were found to give the same ratio as multiple integrations of the signals. The values for the multiple integrations and peak height measurements have an error of ± 1

TABLE 3

RESULTS OF A KINETIC STUDY OF THE DECARBONYLATION OF A 95/5 MIXTURE OF Ia/Ib

Time (min).	Starting I (g)	Recovered I (g)	Isolated II (g)
10	1.000[a]	0.893	0.098
15	1.000[a]	0.866	0.127
20	0.500[b,c]	0.377	0.092
25	0.500[b,c]	0.359	0.114

[a] In 250 ml of benzene. [b] In 125 ml of benzene. [c] A trace of $[(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$ also isolated.

percent unit. The average of 4-6 integrations or 4 peak height measurements was taken.

Preparation of $[(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2]_2$

A suspension of 9 g (30 mmol) of 1-diazo-2-methyl-3,4,5-triphenylcyclopentadiene and 18 g (50 mmol) of $Fe_2(CO)_9$ in 270 ml of benzene was stirred at 40° for 30 min. The mixture was then filtered and the solvent was removed. The residue was extracted with pentane and the solvent was removed from the extract to yield 4.7 g of 2-methyl-3,4,5-triphenylcyclopentadiene. The pentane-insoluble residue was recrystallized from CH_2Cl_2/pentane to afford 4.2 g (35% yield) of $[(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2]_2$, $\nu(C{\equiv}O)$ 1987 vs, 1945 cm^{-1}, $\nu(C{=}O)$ 1773 vs cm^{-1} (CH_2Cl_2 solution).

Preparation of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2CH_3$

The salt $Na[(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2]$ was prepared by stirring a solution of 4.2 g (5.0 mmol) of $[(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2]_2$ in 60 ml of THF with excess 2% sodium amalgam. After 1 h the excess amalgam was removed. A solution of 1.4 g (10 mmol) of CH_3I in 10 ml of THF was added and the resulting mixture was stirred for 3 h. The solvent was removed and the residue was extracted with pentane and filtered through two inches of alumina. The pentane was removed from the extract to afford 3.0 g (70% yield) of the yellow crystals of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2CH_3$.

Preparation of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)[P(C_6H_5)_3](COCH_3)$

A solution of 3.0 g (6.9 mmol) of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2CH_3$ and 1.8 g (6.9 mmol) of $P(C_6H_5)_3$ in 50 ml of CH_3CN was maintained at reflux for 24 h. The solvent was then removed and the residue was dissolved in a minimum amount of benzene and chromatographed on alumina. Elution with benzene afforded a trace of $[(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2]_2$; then elution with CH_2Cl_2 yielded the orange-colored product. The volume of the solution was reduced and 2.8 g (58% yield) of the orange crystals of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)[P(C_6H_5)_3](COCH_3)$ were obtained upon addition of pentane.

Preparation of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)[P(C_6H_5)_3]CH_3$

A solution of 1.6 g (2.3 mmol) of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)[P(C_6H_5)_3](COCH_3)$ in 300 ml of 5/1 benzene/pentane was irradiated for 3.5 h. The solution was then concentrated and chromatographed on alumina. Elution with 3/1 pentane/benzene afforded a red band of the product. The solvent was removed from the effluent and recrystallization of the residue from CH_2Cl_2/pentane afforded 0.78 g (51% yield) of red crystals of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)[P(C_6H_5)_3]CH_3$. Elution with CH_2Cl_2 gave the unreacted acetyl complex.

Preparation of $[(h^5\text{-}1\text{-}CH_3C_9H_6)Fe(CO)_2]_2$

A solution of 26 g (0.20 mol) of 3-methylindene and 40 g (0.20 mol) of $Fe(CO)_5$ in 250 ml of heptane was maintained at reflux for 21 h, filtered, and concentrated. Upon addition of pentane, 5.2 g (11% yield) of the dark red crystals of $[(h^5\text{-}1\text{-}CH_3C_9H_6)Fe(CO)_2]_2$ was obtained, $\nu(C{\equiv}O)$ 1989 vs, 1945 vs cm^{-1}, $\nu(C{=}O)$ 1767 vs cm^{-1} (CH_2Cl_2 solution).

Preparation of $(h^5$-1-CH$_3$C$_9$H$_6$)Fe(CO)$_2$CH$_2$C$_6$H$_5$

The salt Na[h^5-1-CH$_3$C$_9$H$_6$)Fe(CO)$_2$] was obtained by the reduction of 1.7 g (3.5 mmol) of [(h^5-1-CH$_3$C$_9$H$_6$)Fe(CO)$_2$]$_2$ in 60 ml of THF with excess 2% sodium amalgam. After stirring for 1 h and removal of excess amalgam, 0.89 g (7.0 mmol) of C$_6$H$_5$CH$_2$Cl in 15 ml of THF was added and the resulting mixture was stirred for 3 h. This solution was filtered, the solvent was removed and the residue was chromatographed on alumina. Elution with pentane afforded the orange-colored product. After removal of the pentane from the effluent, 0.88 g (38% yield) of (h^5-1-CH$_3$C$_9$H$_6$)Fe(CO)$_2$CH$_2$C$_6$H$_5$ was obtained.

Preparation of $(h^5$-1-CH$_3$C$_9$H$_6$)Fe(CO)[P(C$_6$H$_5$)$_3$](COCH$_2$C$_6$H$_5$)

A solution of 0.83 g (2.5 mmol) of (h^5-1-CH$_3$C$_9$H$_6$)Fe(CO)$_2$CH$_2$C$_6$H$_5$ and 0.66 g (2.5 mmol) of P(C$_6$H$_5$)$_3$ in 50 ml of CH$_3$CN was kept at reflux for 70 h. Extensive decomposition was apparent. The solvent was removed and the residue was chromatographed on alumina. Elution with pentane afforded the unreacted starting materials; elution with 1/1 benzene/CH$_2$Cl$_2$ gave the red product. The solvent was removed and the product was recrystallized from ether/hexane to give 0.77 g (52% yield) of orange crystals of (h^5-1-CH$_3$C$_9$H$_6$)Fe(CO)[P(C$_6$H$_5$)$_3$]-(COCH$_2$C$_6$H$_5$).

Preparation of $(h^5$-1-CH$_3$C$_9$H$_6$)Fe(CO)[P(C$_6$H$_5$)$_3$]CH$_2$C$_6$H$_5$

A solution of 1.2 g (2.0 mmol) of (h^5-1-CH$_3$C$_9$H$_6$)Fe(CO)[P(C$_6$H$_5$)$_3$]-(COCH$_2$C$_6$H$_5$) in 250 ml of 4/1 benzene/pentane was irradiated for 1.5 h. The solution was then concentrated and chromatographed on alumina. Elution with 1/1 pentane/benzene afforded the product, whereas elution with CH$_2$Cl$_2$ yielded the unreacted starting material. Removal of the solvent from the first effluent furnished 0.56 g (48% yield) of (h^5-1-CH$_3$C$_9$H$_6$)Fe(CO)[P(C$_6$H$_5$)$_3$]CH$_2$C$_6$H$_5$.

Preparation of h^5-C$_5$H$_5$Fe(CO)[*S*-(+)-(C$_6$H$_5$)$_2$PCH$_2$CH(C$_6$H$_5$)C$_2$H$_5$](COCH$_3$)

A solution of 1.0 g (3.1 mmol) of *S*-(+)-(C$_6$H$_5$)$_2$ PCH$_2$CH(C$_6$H$_5$)C$_2$H$_5$ and 0.63 g (3.1 mmol) of h^5-C$_5$H$_5$Fe(CO)$_2$CH$_3$ in 25 ml of THF was maintained at reflux for 72 h. The solvent was then removed and the residue was chromatographed on a 3 × 35 cm column of alumina. Elution with pentane gave unreacted h^5-C$_5$H$_5$Fe(CO)$_2$CH$_3$; then elution with CHCl$_3$ and removal of the solvent afforded 1.2 g (73% yield) of the orange oil of h^5-C$_5$H$_5$Fe(CO)[*S*-(+)-(C$_6$H$_5$)$_2$PCH$_2$CH(C$_6$H$_5$)C$_2$H$_5$](COCH$_3$).

Preparation of h^5-C$_5$H$_5$Fe(CO)[*S*-(+)-(C$_6$H$_5$)$_2$PCH$_2$CH(C$_6$H$_5$)C$_2$H$_5$]CH$_3$

A solution of 1.0 g (2.0 mmol) of h^5-C$_5$H$_5$Fe(CO)[*S*-(+)-(C$_6$H$_5$)$_2$PCH$_2$CH-(C$_6$H$_5$)C$_2$H$_5$](COCH$_3$) in 250 ml of 4/1 benzene/pentane was irradiated under nitrogen for 3 h. The solvent was removed and the residue was chromatographed on a 3 × 30 cm column of alumina. Elution with 4/1 pentane/benzene afforded after removal of the solvent 0.55 g (55% yield) of the orange oil of h^5-C$_5$H$_5$Fe-(CO)[*S*-(+)-(C$_6$H$_5$)$_2$PCH$_2$CH(C$_6$H$_5$)C$_2$H$_5$]CH$_3$. Elution with CH$_2$Cl$_2$ gave the unreacted acetyl complex.

Preparation of h^5-C$_5$H$_5$Fe(CO)[P(CH$_3$)(C$_6$H$_5$)(β-C$_{10}$H$_7$)]CH$_3$

A solution of 1.3 g (6.5 mmol) of h^5-C$_5$H$_5$Fe(CO)$_2$CH$_3$ and 1.6 g (6.5

mmol) of $P(CH_3)(C_6H_5)(\beta\text{-}C_{10}H_7)$ in 300 ml of petroleum ether was photolyzed under nitrogen for 2 h. The solvent was then removed and the residue was chromatographed on alumina. Elution with pentane yielded unreacted $h^5\text{-}C_5H_5Fe(CO)_2CH_3$, whereas elution with benzene gave after removal of the solvent 1.4 g (54% yield) of the red oil of $h^5\text{-}C_5H_5Fe(CO)[P(CH_3)(C_6H_5)(\beta\text{-}C_{10}H_7)]CH_3$.

Results and discussion

Design of the system

Our design of a satisfactory system of the general formula (h^5-cyclopentadienyl)Fe(CO)(L)(COR) for a stereochemical study of the decarbonylation is based on the construction of diastereomers through the generation of two chiral centers in the above composition. One of these centers is the metal present in a pseudotetrahedral environment. The second asymmetric center may be introduced into one of the ligands h^5-cyclopentadienyl, L or COR. An (h^5-cyclopentadienyl)Fe(CO)(L)(COR) complex with asymmetry in the acyl moiety was the subject of an earlier publication [18]. One of the more severe limitations of such a model is that cleavage of the M—COR bond (or the M—R bond derived therefrom) with extrusion of the COR (or R) moiety leaves only one chiral center in the resultant metal complex. Thus diastereomers are no longer possible. This of course does not apply to the decarbonylation; however, it does limit the number of reactions at metal—carbon σ-bonds that can be investigated with respect to their stereochemistry.

The above problem can be circumvented by the introduction of asymmetry into either h^5-cyclopentadienyl or L. Both approaches were tried in this work. It might appear a priori that the former approach would be the more successful, since h^5-cyclopentadienyl rings are firmly bound to the iron. In contrast, ligands L such as $P(C_6H_5)_3$ are known to be replaced through substitution reactions in complexes of the type (h^5-cyclopentadienyl)Fe(CO)(L)R [33].

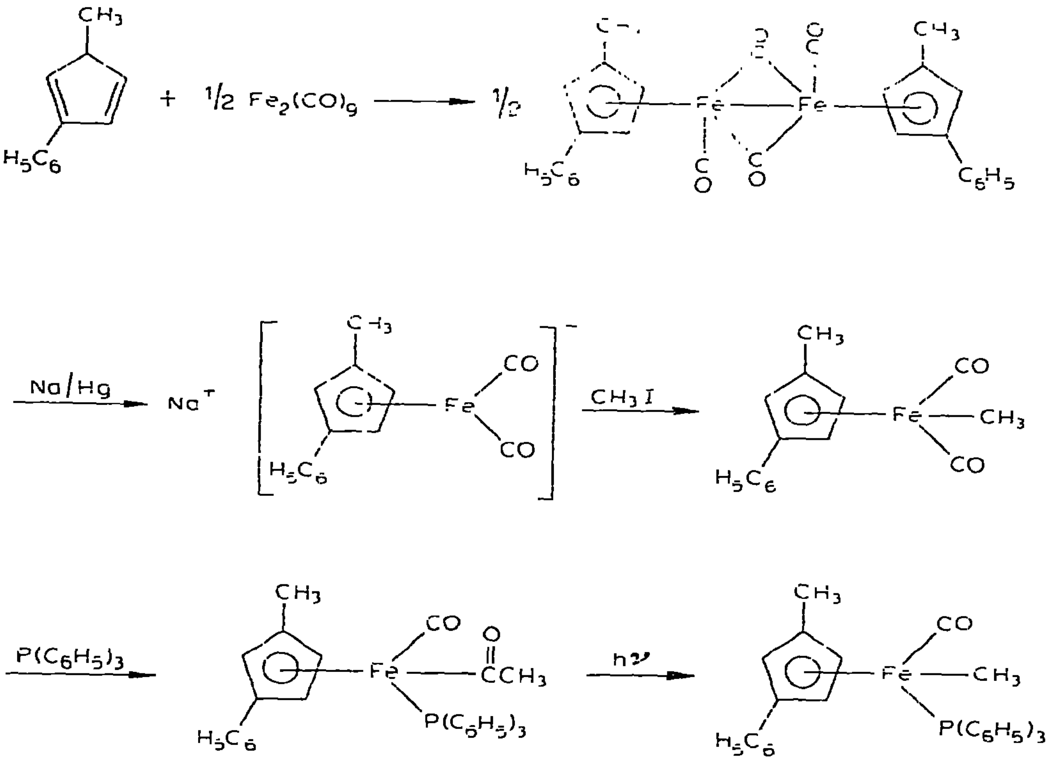
Of the several acyl and alkyl complexes of the general formulas (h^5-cyclopentadienyl)Fe(CO)(L)(COR) and (h^5-cyclopentadienyl)Fe(CO)(L)R prepared in this study, the most satisfactory system for the proposed investigation proved to be $(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3](COCH_3)$ (I)—$(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)[P(C_6H_5)_3]CH_3$ (II). A study on this system comprises most of the Results and discussion section of this paper. The remaining systems, which turned out to be either less satisfactory than I—II or totally unsatisfactory, are described briefly at the end of this discussion.

Synthesis, characterization and properties of I and II and of their diastereomers

The synthesis of the organoiron complexes containing an $h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3$ ring is given in Scheme 1.

The dinuclear compound $[(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$ was isolated in 23% yield (or higher, up to 65%, if the recovered substituted cyclopentadiene is used again) as a dark purple solid. It was characterized through IR spectroscopy in the $\nu(C{\equiv}O)$ region. Reduction of this complex in THF with sodium amalgam and treatment of the resulting solution with CH_3I gave $(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2CH_3$ in 79% yield. The iron alkyl was characterized by IR and ^1H

SCHEME 1



(I)

(II)

NMR spectroscopy and mass spectrometry, as shown in Table 4. Through the action of $P(C_6H_5)_3$ in CH_3CN at reflux this complex was converted to I in 53% yield. The photochemical decarbonylation of I in benzene afforded good yields of II. Both I and II were characterized by elemental analyses (Table 1) and IR and ^1H NMR spectroscopy (Table 4).

The complexes I and II possess two chiral centers, i.e. the metal and the unsymmetrically disubstituted *pentahapto*-cyclopentadienyl ring, and hence are present as mixtures of two diastereomerically related pairs of enantiomers, (*RR*)-I-(*SS*)-I and (*RS*)-I-(*SR*)-I (designated as Ia and Ib) and (*RR*)-II-(*SS*)-II and (*RS*)-II-(*SR*)-II (designated as IIa and IIb). These isomers are drawn in Fig. 1, but the relationship between the designation a and b and the absolute configuration is not known *. For simplicity, the two enantiomeric pairs will be labeled as diastereomers a and b. This is because under achiral conditions employed here, reactions of enantiomers proceed through energetically identical pathways.

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* The priority sequence for determining *R* and *S* configuration for chiral iron is taken to be $P(C_6H_5)_3$ > *h*⁵-cyclopentadienyl > CO > $COCH_3$ > CH_3. The rules for establishing the *R* and *S* designations associated with the chirality of π-complexes are given in ref. 34.

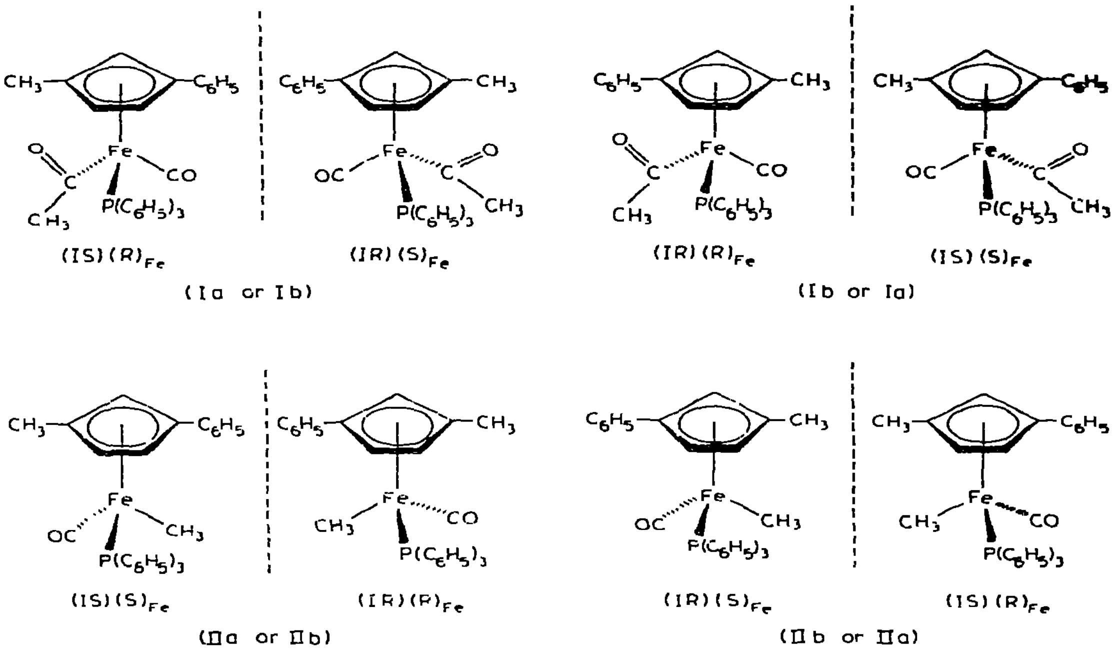

Fig. 1. The four stereoisomers of I and II.

The diastereomers of I, Ia and Ib, and of II, IIa and IIb, have readily distinguishable ^{1}H NMR spectra (Table 4). The NMR spectra of a 95/5 and a 0/100 mixture of Ia/Ib in the region τ 5-10 are shown in Fig. 2 The NMR spectra of a 97/3 and an 8/92 mixture of IIa/IIb in the same region are reproduced in Fig. 3. It is readily seen that the two methyl groups and the three cyclopentadienyl ring protons are diastereotopic by external comparison in both I and II. By integration of the C_5H_3 signals between τ 5.20 and 6.28 in I and of the signals due to the methyl groups on the cyclopentadienyl ring at τ 8.22 and 8.53 in II, the ratios of diastereomers in mixtures can be readily determined.

The diastereomers of I were separated by a combination of chromatography on alumina and fractional crystallization of the resulting enriched mixtures from benzene/pentane. Fractional crystallization of 50/50 mixtures was also tried, but unsuccessfully, as a separation technique. The more soluble diastereomer Ia is eluted faster from a column of alumina and may be obtained readily in 95% purity by repetitive chromatography. A small amount of diastereomerically pure Ia was obtained by careful crystallization of a 95/5 mixture of Ia/Ib. Diasteromerically pure Ib can be isolated by successive crystallizations of the accumulated back fractions from the above-mentioned chromatography of Ia/Ib. Both procedures are described in detail in the Experimental section.

The diastereomers of II were too unstable toward alumina to allow their separation by repetitive column chromatography. However, mixtures enriched in IIa and IIb were obtained from the stereospecific decarbonylation of Ia and Ib, respectively, as described in the Experimental section. To minimize the slow epimerization of IIa and IIb under the photolytic conditions, solutions of Ia and

TABLE 4

SPECTROSCOPIC DATA FOR NEW h^5-CYCLOPENTADIENYL COMPLEXES

(h^5-cyclopentadienyl)	L	R	IR(cm^{-1})[b]	
			ν(C≡O)	ν(C=O)
1-CH_3-3-$C_6H_5C_5H_3$	CO	CH_3 [a]	1997, 1945 [c]	
1-CH_3-3-$C_6H_5C_5H_3$	P$(C_6H_5)_3$	$COCH_3$ (I)	1914	1595
1-CH_3-3-$C_6H_5C_5H_3$	P$(C_6H_5)_3$	CH_3 (II)	1904 [c]	
1-CH_3-2,3,4-$(C_6H_5)_3C_5H$	CO	CH_3	2003, 1945	
1-CH_3-2,3,4-$(C_6H_5)_3C_5H$	P$(C_6H_5)_3$	$COCH_3$	1914	1590
1-CH_3-2,3,4-$(C_6H_5)_3C_5H$	P$(C_6H_5)_3$	CH_3	1901 [c]	
1-$CH_3C_9H_6$	P$(C_6H_5)_3$	$COCH_2C_6H_5$	1912 [c]	1612 [c]
1-$CH_3C_9H_6$	P$(C_6H_5)_3$	$CH_2C_6H_5$	1907	
C_5H_5	S-(+)-$(C_6H_5)_2PCH_2CH(C_6H_5)C_2H_5$	$COCH_3$	1917	1590
C_5H_5	S-(−)-$(C_6H_5)_2PCH_2CH(C_6H_5)C_2H_5$	CH_3	1905	
C_5H_5	P$(CH_3)(C_6H_5)(\beta\text{-}C_{10}H_7)$	CH_3	1903 [c]	

[a] Mass spectrum (AEI Model MS-9 spectrometer, at 70eV, source temp. 70°)· P^+(7), P^+—CO(16), P^+—2CO—$C_{12}H_{11}Fe(CO)_2CH_3$, intensities relative to *m/e* 56 = 100 given in parentheses. [b] In $CHCl_3$ solution unless internal standard. Aromatic C_6H_x protons omitted. Relative intensities in parentheses. Abbreviations: s, [h] *J*(P—H) = 6 5 Hz. [i] Protons 2 and 3 of C_9H_6. [j] AB quartet, *J*(H—H) = 16 Hz. [k] *J*(H—H) = 7 Hz. [l] *J*(P—H) =

Ib were irradiated for short periods of time (5-15 min.) and the product II was separated from I by chromatography. The acetyl I was then rephotolyzed and again the alkyl II was separated. This procedure was repeated to accumulate larger amounts of 85/15 and 8/92 mixtures of IIa/IIb. A 97/3 mixture of IIa/IIb as well as diasteromerically pure IIa were obtained by fractional crystallization of the 85/15 mixture of IIa/IIb. An 8/92 mixture of IIa/IIb was isolated from the 5 minute decarbonylation of pure Ib. No attempt was made at obtaining diastereomerically pure IIb.

Stereospecificity of the photochemical decarbonylation of Ia and Ib

The diastereomeric acetyls Ia and Ib undergo photochemical decarbonylation at 3500 Å to afford the corresponding methyl derivatives enriched in IIa and IIb, respectively. Mixtures of Ia/Ib of different percent composition, determined by NMR spectroscopy, were photolyzed for various time intervals and the unreacted acetyl and product methyl complexes were separated by chromatography. The ratios of the recovered Ia/Ib and the product IIa/IIb were determined by NMR spectroscopy. The results of these experiments are given in Table 2.

(*Table 4 continued*)

^{1}H NMR(τ)^d		
(h^5-C_5H_5)	R	L
8.04s(3), CH_3C_5; 5.35m(1), 5.00m(2), C_5H_3	9.92s(3), CH_3	
Ia: 8.32s(3), CH_3C_5; 6.28m(1), 5.25m(1), 5.20m(1), C_5H_3	7.72s(3), $COCH_3$	
Ib: 8.44s(3), CH_3C_5: 5.83m(1), 5.55m(1), 5.35m(1), C_5H_3	7.96s(3), $COCH_3$	
IIa: 8.22s(3), CH_3C_5; 6.19m(1), 5.90m(1), 5.73m(1), C_5H_3 ^{e}	9.91d ^{g}(3), CH_3 ^{e}	
IIb: 8.53s(3), CH_3C_5; 6.79m(1), 5.70m(1), 5.6m(1), C_5H_3 ^{e}	9.82d ^{g}(3), CH_3 ^{e}	
8.38s(3), CH_3C_5; 5.55s(1), C_5H	9.55s(3), CH_3	
8.22s(3), CH_3C_5: 5.30s, 5.22s(1), C_5H ^{e}	7.35s(3), $COCH_3$ ^{e}	
8.71s, 8.62s(3), CH_3C_5: 5.97s, 5.80s(1), C_5H ^{i}	10.28d ^{h}, 10.22d ^{h}(3), CH_3 ^{f}	
7.82s(3), CH_3C_9; 5.63m, 5.32m(2), C_9H_2 ^{i}	6.95, 6.51 ^{j}(2), $COCH_2$	
7.15s(3), CH_3C_9; 5.95m, 5.20m(2), C_9H_2 ^{i}	8 2m, 7.7m(2), CH_2	
5.77s, 5.70s(5), C_5H_5	7.53s, 7.42s(3), $COCH_3$	9.52t ^{k}(3) CH_3C; 8.68m(2), CH_2C; 7.3m(3), CH_2P, CH
5.92s(5), C_5H_5	10.18d ^{l}, 10.17d ^{l}(3), CH_3	9.58t ^{k}(3), CH_3C; 8.8m(2), CH_2C; 7.5m(3), CH_2P, CH
5.88s(5), C_5H_5	10.23d ^{h}(3), CH_3	8.28d ^{m}(3), CH_3P

CH_3(17), $C_{12}H_{10}Fe^+$(32), $C_9H_6Fe^+$, $C_{13}H_{14}^+$(440), $C_8H_9FeO^+$(12). Only peaks of $m/e > 160$ given, P = indicated otherwise. ^{c} In CH_2Cl_2 solution. ^{d} In $CDCl_3$ solution unless noted otherwise, $Si(CH_3)_4$ (TMS) singlet; d, doublet; t, triplet; m, multiplet. ^{e} In C_6D_6 solution. ^{f} In CH_2Cl_2 solution ^{g} J(P—H) = 6.4 Hz. 6.2 Hz. ^{m} J(P—H) = 8.5 Hz.

Four points of interest emerge upon examination of the above data. First, the observed stereospecificity of the decarbonylation decreases with longer periods of the irradiation; this has been demonstrated for a 95/5 mixture of Ia/Ib which was irradiated for 5, 15, and 40 min. in benzene solution. A similar decrease in stereospecificity of the photochemical decarbonylation has been observed for optically active h^5-$C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ by Brunner and Strutz [35] and by Davison and Martinez [36]. Second, the stereospecificity of the decarbonylation for 5 min. in benzene solution is the same (i.e. 84%) for Ib as for Ia (actually 95/5 Ia/Ib). Therefore, the rates of the decarbonylation of Ia and Ib are equal (also vide infra). Third, the decarbonylation of pure Ib proceeds with the same stereospecificity (84% for 5 min.) in benzene and in THF solutions. The rates of the thermal decarbonylation of (RCO)Mn(CO)$_5$ [3] and *trans*-h^5-C_5H_5Mo-$(CO)_2L(COCH_3)$ [37] have also been shown to be essentially solvent independent. Fourth, the ratio of Ia/Ib in the acetyl recovered from each reaction is identical with the initial Ia/Ib ratio. This observation shows that I is configurationally stable when dissolved in benzene, toward the alumina chromatography, and under the photochemical conditions employed in decarbonylation. Furthermore, since no change in the ratio of Ia/Ib was observed up to 50% decarbonylation, the rate of the reaction must be the same for both diastereomers, as has already been mentioned above.

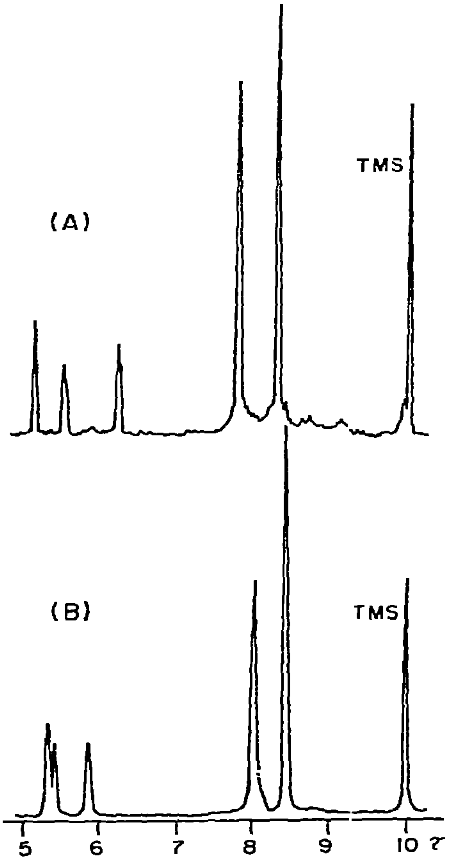

Fig. 2. The 100MHz ^{1}H NMR spectra of (A) a 95/5 mixture of Ia/Ib and (B) pure Ib in CDCl$_3$solution.

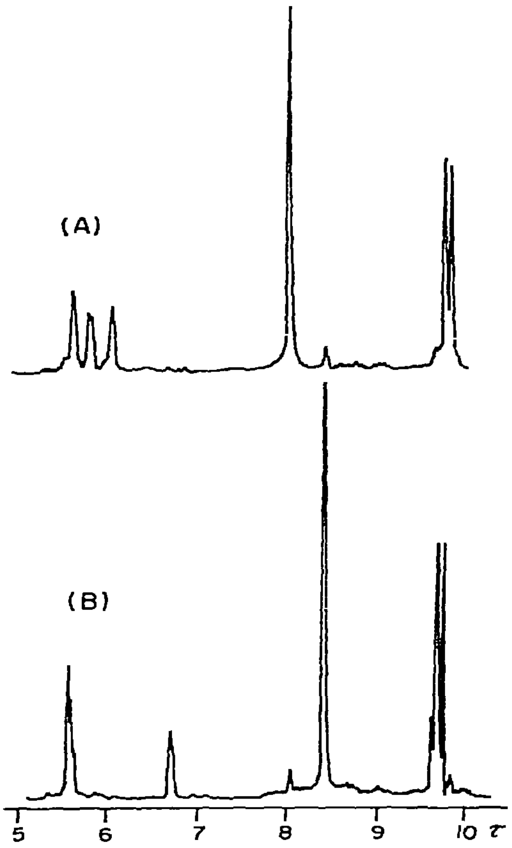

Fig. 3. The 100 MHz ^{1}H NMR spectra of (A) a 97/3 mixture of IIa/IIb and (B) an 8/92 mixture of IIa/IIb in C$_6$D$_6$ solution.

The diastereomers of II are stable in benzene and THF both in the dark and in ordinary laboratory light. However, epimerization of IIa and IIb does occur under the photochemical reaction conditions of decarbonylation. This was demonstrated by photolyzing a 70/30 mixture of IIa/IIb in benzene solution (vide infra). No significant changes in the ratio of IIa/IIb were observed during chromatography.

The results obtained for the photochemical decarbonylation of Ia and Ib are discussed conveniently in the context of the reactions comprising Scheme 2*. All of the transformations I → II are considered to be irreversible under the conditions employed in this study; precedent for this assumption exists in the literature [33]. Also, since the decarbonylation proceeds with $\geqslant$ 84% stereospecificity, $k_{\rm I}$ must be considerably greater than k_x.

In order to test the validity of Scheme 2 and to calculate the constants $k_{\rm I}$ and $k_{\rm II}$, we investigated kinetically under the same conditions the decarbonylation of a 95/5 mixture of Ia/Ib and the photochemical epimerization of a 70/30 mixture of IIa/IIb. If k_x is insignificant in this scheme, then the value of $k_{\rm II}$

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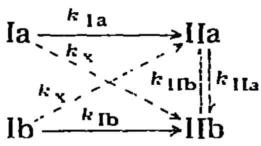
[*] See Note added in proof, p. 415.

from the decarbonylation experiment should equal the value of k_{II} from the epimerization experiment. However, the value of k_{II} from the decarbonylation will be larger than that from the epimerization if the k_x-path is important.

SCHEME 2



The two reactions were investigated only for short periods of time. The appearance of $[(h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3)Fe(CO)_2]_2$ at longer reaction times showed that some decomposition was occurring in these systems. Additionally, the necessity of separating I and II (or of purifying II) by column chromatography for NMR analyses unavoidably reduced the accuracy of the experimental data.

The results of these experiments are presented in Tables 3 and 5 for the decarbonylation and in Table 6 for the epimerization. The entire decarbonylation process in Scheme 2 was analyzed as a series of first-order reactions, with the following assumptions in the treatment of the data. The constants k_{Ia} and k_{Ib} were taken to be equal on the basis of the observations described earlier (see above). Because II epimerizes to a 50/50 mixture of IIa/IIb, k_{IIa} was set equal to k_{IIb}. Furthermore, k_x was ignored because $k_I \gg k_x$, as has already been stated. Finally, the photochemically induced decarbonylation of I and the epimerization of II were both assumed to be first-order processes. For comparison, thermal decarbonylation of metal—acyl complexes proceeds by the loss of a terminal CO in the rate determining step [1]; similarly, a terminal CO is lost in the

TABLE 5

EXPERIMENTAL AND CALCULATED[a] DATA FOR THE DECARBONYLATION OF A 95/5 MIXTURE OF Ia/Ib IN BENZENE SOLUTION

Time (min.)	Concentration × 10^2 (M) Ia	Ib	IIa	IIb	Ia/Ib	Yield of II (%)	IIa/IIb
0	0.698	0.0367	-	-	95/5	0	-
10	0.626 (0.626)	0.0330 (0.0330)	0.0639 (0.0623)	0.0122 (0.0133)	95/5 (95/5)	10 (10)	84/16 (82/18)
15	0.605 (0.593)	0.0319 (0.0313)	0.0748 (0.0859)	0.0237 (0.0245)	95/5 (95/5)	13 (15)	76/24 (78/22)
20	0.562 (0.562)	0.0296 (0.0296)	0.106 (0.106)	0.0371 (0.0373)	95/5 (95/5)	19 (19)	74/26 (74/26)
25	0.530 (0.532)	0.0279 (0.0281)	0.126 (0.124)	0.0513 (0.0509)	95/5 (95/5)	24 (24)	71/29 (71/29)

[a] In parentheses; calculated using $k_I = 2 \times 10^{-4}$/s and $k_{II} = 6 \times 10^{-4}$/s.

TABLE 6

EXPERIMENTAL AND CALCULATED[a] STEREOCHEMICAL DATA FOR THE EPIMERIZATION OF A 70/30 MIXTURE OF IIa/IIb IN BENZENE SOLUTION

Time (min.)	IIa/IIb
0	70/30
5	64/36 (64/36)
10	60/40 (59/41)
15	55/45 (56/44)
20	54/46 (54/46)

[a] In parentheses: calculated using $k_{II} = 6 \times 10^{-4}$/s.

photochemical decarbonylation of h^5-$C_5H_5Fe(CO)_2(^{13}COCH_3)$ [38]. The foregoing assumptions simplify the reaction scheme to that shown below (Scheme 3).

SCHEME 3

$$\begin{tikzcd}
\mathrm{Ia} \arrow[r, "k_I"] & \mathrm{IIa} \arrow[d, shift left, "k_{II}"] \\
\mathrm{Ib} \arrow[r, "k_I"] & \mathrm{IIb} \arrow[u, shift left, "k_{II}"]
\end{tikzcd}$$

The concentrations of Ia, Ib, IIa and IIb were determined from the amounts of total I and II isolated after chromatography (Table 3) and from the ratios of Ia/Ib and IIa/IIb elucidated by NMR spectroscopy (Table 5). Using a computer program for a second-order numerical integration of the reactions in Scheme 3, values of k_I and k_{II} were varied to provide the best fit for the experimental and calculated concentrations of the four iron complexes. The results are given in Table 5. The constants obtained in this manner are $k_I = 2 \times 10^{-4}$/s and k_{II} (accompanying the decarbonylation of I) = 6×10^{-4}/s.

The constant k_{II} was then calculated using the data from the experiment on the photochemically induced epimerization of II. The computation entailed the use of a second-order numerical integration of a reversible first-order reaction to obtain the best fit of experimental and calculated ratios of IIa/IIb (Table 6). The derived value of k_{II}, 6×10^{-4}/s, is identical with that obtained using the data from the decarbonylation experiments.

The above results do not unequivocally rule out some contribution from the k_x-path in Scheme 2*, although such a pathway must be minor compared to the stereospecific decarbonylation—epimerization sequence. We would suggest that the decarbonylation of I is most probably a completely stereospecific (100%) reaction. The value of > 84% stereospecificity is the lower limit imposed by experimental constraints, since solutions of I must be irradiated long enough to yield sufficient product for NMR analysis. Following the formation of II, epimerization occurs under these photolytic conditions.

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* Considerable absorption of the light causing photoepimerization of II by I will result in a lower experimental value of k_{II} in the decarbonylation experiment.

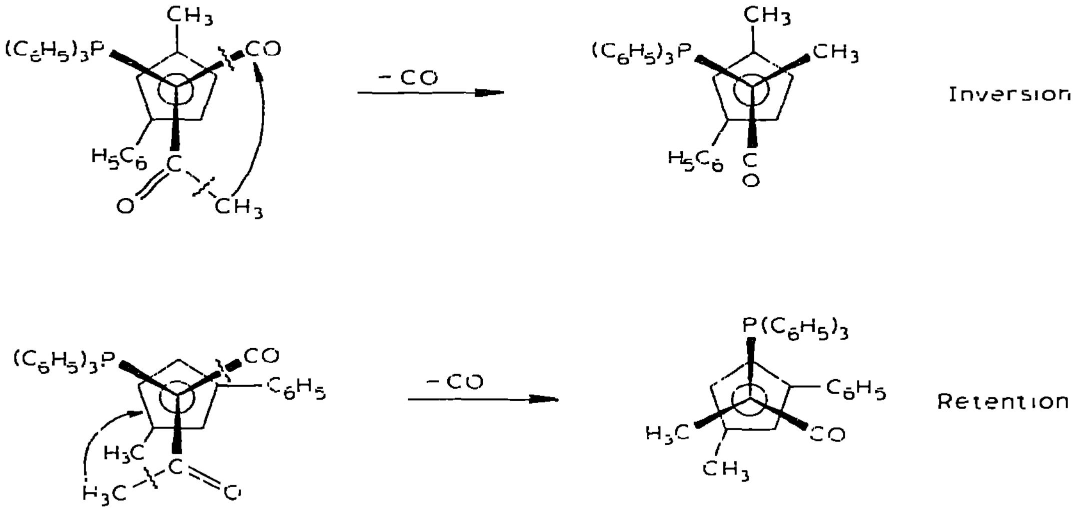

Fig. 4. Concerted mechanisms of the decarbonylation of I with inversion and retention of configuration at the iron center.

Mechanistic information derived from the decarbonylation of Ia and Ib

Two alternatives, inversion or retention at the metal, are possible for the decarbonylation of I. Furthermore, there are two limiting mechanistic situations in each case. The reaction may proceed in a concerted fashion, with the photochemically excited CO being replaced by the migrating methyl group as depicted in Fig. 4 (concerted mechanism). Alternatively, however, the Fe—CO bond may break prior to the migration of the CH_3 fragment with either inversion or retention at the iron center (dissociative mechanism).

We cannot differentiate between concerted and dissociative mechanisms from the data obtained in this work. However, if the dissociative mechanism is operative, then the present stereochemical result demonstrates that the intermediate species with reduced coordination number of iron, i.e. $(h^5\text{-1-}CH_3\text{-3-}C_6H_5C_5H_3)Fe[P(C_6H_5)_3](COCH_3)$, possesses high configurational stability and does not adopt planar geometry around the metal. Whether the stereospecific decarbonylation of I involves retention or inversion at iron can be elucidated only with the aid of X-ray crystallography. However, it has been shown recently that the photochemical decarbonylations of $(+)_{546}\text{-}h^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3](COCH_3)$ [35] and $R\text{-}(+)\text{-}h^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3](COC_2H_5)$ [36] proceed with inversion of configuration at the iron center. Thus it is very likely that the I → II transformation also entails inversion at the metal.

The photochemical epimerization of II may be either a dissociative or a nondissociative process. A dissociative pathway may involve any one of the four ligands bonded to the metal. Of the four, $P(C_6H_5)_3$ is probably the most likely candidate to part with the metal judged from the related behavior reported in the literature. Thus, the dissociation of $P(C_6H_5)_3$ has been proposed to account for the epimerization of $h^5\text{-}C_5H_5Mn(NO)[P(C_6H_5)_3][(-)\text{-}COOC_{10}H_{19}]$ in solution [39]. Furthermore, $h^5\text{-}C_5H_5Fe(CO)[P(C_6H_5)_3]CH_3$ reacts with $P(OR)_3$ ($R = CH_3$, $n\text{-}C_4H_9$, or C_6H_5) to give $h^5\text{-}C_5H_5Fe(CO)[P(OR)_3]CH_3$ [33], probably also via dissociation of $P(C_6H_5)_3$. In a nondissociative process, epimerization may result from absorption of a quantum of incident light by the alkyl complex leading to an intramolecular ligand scrambling.

Other systems

Two other new dinuclear complexes of the general formula $[(h^5\text{-cyclopentadienyl})Fe(CO)_2]_2$ where h^5-cyclopentadienyl is an unsymmetrically substituted *pentahapto*-cyclopentadienyl ring were prepared in this study. The complex $[(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)_2]_2$ resulted upon treatment of the appropriate diazocyclopentadiene with $Fe_2(CO)_9$, whereas $[(h^5\text{-}1\text{-}CH_3C_9H_6)Fe(CO)_2]_2$ was obtained by the reaction of 3-methylindene with $Fe(CO)_5$ in heptane at reflux. Both syntheses are described in detail in the Experimental section. It is noteworthy that attempted reactions of 2-methyl-3,4,5-triphenylcyclopentadiene with each of $Fe(CO)_5$ at 70—85° and $Fe_2(CO)_9$ at room temperature resulted in the recovery of unreacted substituted cyclopentadiene. More forcing conditions were not tried since reactions between $Fe(CO)_5$ and cyclopentadienes with bulky substituents often lead to the formation of the appropriate ferrocenes rather than $[(h^5\text{-cyclopentadienyl})Fe(CO)_2]_2$ [40].

The derivatives $(h^5\text{-cyclopentadienyl})Fe(CO)_2R$, $(h^5\text{-cyclopentadienyl})Fe(CO)[P(C_6H_5)_3](COR)$ and $(h^5\text{-cyclopentadienyl})Fe(CO)[P(C_6H_5)_3]R$ were prepared by reactions analogous to those for the corresponding complexes containing the $h^5\text{-}1\text{-}CH_3\text{-}3\text{-}C_6H_5C_5H_3$ ring. The monocarbonyls were characterized by IR and ^1H NMR spectroscopy, as shown in Table 4.

The NMR spectra of the diastereomers of each of $(h^5\text{-}1\text{-}CH_3C_9H_6)Fe(CO)[P(C_6H_5)_3](COCH_2C_6H_5)$ and $(h^5\text{-}1\text{-}CH_3C_9H_6)Fe(CO)[P(C_6H_5)_3]CH_2C_6H_5$ appear to be identical, thus precluding the use of this system for a stereochemical study of the decarbonylation. The diastereomers of $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)[P(C_6H_5)_3]CH_3$ have sufficiently different NMR spectra to determine their ratios in mixtures; however, in the NMR spectrum of the corresponding $(h^5\text{-}1\text{-}CH_3\text{-}2,3,4\text{-}(C_6H_5)_3C_5H)Fe(CO)[P(C_6H_5)_3](COCH_3)$, only the single proton on the cyclopentadienyl ring gives rise to nonequivalent chemical shifts for the diastereomers. Because of this near degeneracy and a limited solubility of the acetyl compound in the usual NMR solvents, no stereochemical investigation was undertaken on its decarbonylation reaction.

Two types of complexes of the general formula $h^5\text{-}C_5H_5Fe(CO)(L)R$ with L being a chiral tertiary phosphine were examined in this work. One contained $P(CH_3)(C_6H_5)(\beta\text{-}C_{10}H_7)$, with a chiral phosphorus, and the other $S\text{-}(+)\text{-}(C_6H_5)_2PCH_2CH(C_6H_5)C_2H_5$, with an asymmetric carbon. The complexes were prepared by standard procedures, as described in the Experimental section. Their IR and ^1H NMR spectra are presented in Table 4.

Again, these systems proved to be unsuitable for a study of their respective photochemical decarbonylations by ^1H NMR spectroscopy. The spectra of $h^5\text{-}C_5H_5Fe(CO)[P(CH_3)(C_6H_5)(\beta\text{-}C_{10}H_7)]CH_3$ appear to be identical, and those of $h^5\text{-}C_5H_5Fe(CO)[S\text{-}(+)\text{-}(C_6H_5)_2PCH_2CH(C_6H_5)C_2H_5]CH_3$ nearly identical, for both diastereomers.

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[*] *Note added in proof (see p. 410).* The rate of a photochemical reaction depends on the quantum yield and on the number of einsteins absorbed by the reactant in unit volume and unit time: see, for example, V. Balzani and V. Carassiti, "Photochemistry of Coordination Compounds", Academic Press, New York, 1970, pp. 11-12. The so-called "rate constants", $k_{\rm I}$, $k_{\rm II}$, and $k_{\rm X}$, used in this paper were calculated as if the reactions studied were thermal, not photochemical. Thus, although the relative values of these "rate constants" are informative, the absolute numbers should be given no photochemical significance.