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CHIRAL IRON COMPLEXES (η^5-C_5H_4CH(Ph)Me)Fe(CO)(L)X (L = PHOSPHINE, PHOSPHITE; X = ACYL, ALKYL, HALIDE, HYDRIDE)

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Summary

The complex [(η^5-C_5H_4CH(Ph)Me)Fe$(CO)_2]_2$, containing a chiral η^5-C_5H_4CH(Ph)Me ligand, was prepared by reaction of $Fe_2(CO)_9$ with α-phenethylcyclopentadiene and converted to (η^5-C_5H_4CH(Ph)Me)Fe$(CO)_2$X where X = I, Br, Cl, and Me by standard procedures. Reaction of (η^5-C_5H_4CH(Ph)Me)Fe$(CO)_2$Me with PPh_3 in MeCN at reflux afforded (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me) as a ca. 50/50 mixture of diastereomerically related pairs of enantiomers (diastereomers), which were substantially (95/5) separated by chromatography. Photochemical decarbonylation of isomerically enriched (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me) gave partly epimerized (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me and resulted in the recovery of the acetyl complex of unchanged diastereomeric composition. Photolysis of (η^5-C_5H_4CH(Ph)Me)Fe$(CO)_2$X (X = I, Br) and PPh_3 or $PTol_3$ (L) yielded (η^5-C_5H_4CH(Ph)Me)Fe(CO)(L)X as 50/50 mixtures of diastereomers, which were substantially (95/5) separated. The iodo diastereomers are configurationally stable in C_6D_6 at 25°C, but equilibrate at 72°C to ca. 50/50 mixtures. Reaction of (η^5-C_5H_4CH(Ph)Me)Fe$(CO)_2$I with $LiAlH_4$ in the presence of L, or of (η^5-C_5H_4CH(Ph)Me)Fe(CO)(L)I with $LiAlH_4$ (L = PPh_3, $PTol_3$, PCy_3, $P(OPh)_3$, $P(OEt)_3$, ETPB), yielded (η^5-C_5H_4CH(Ph)Me)Fe(CO)(L)H as oils of varying degree of stability. Diastereomers of (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H could not be separated chromatographically, and reactions of diastereomerically enriched (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I with $LiAlH_4$, Super Hydride, or K- or L-Selectride afforded a 50/50 isomeric mixture of (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H. The product reacts with $PTol_3$ in C_6D_6 at 25°C to give a 75/25 mixture of (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H and (η^5-C_5H_4CH(Ph)Me)Fe(CO)($PTol_3$)H. All new complexes were characterized by a combination of elemental analysis, IR and NMR (^{1}H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$) spectroscopy, and mass spectrometry. Analysis of diastereomeric mixtures was made by ^{1}H NMR spectroscopy.

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Introduction

Previous papers from this laboratory were concerned with the use of diastereomeric complexes of the type (η^5-C_5H_3-1-Me-3-Ph)Fe(CO)(L)X (X = alkyl, acyl, halide) to probe stereochemistry at iron of reactions that disrupt the Fe–X bond [1–3]. In general, it was possible to derive useful mechanistic information from those studies, although substantial asymmetric induction was observed in some cases.

In an attempt to avoid asymmetric induction in reactions that occur at the chiral metal center, we turned our attention to a structurally somewhat different type of iron complex, viz. (η^5-C_5H_4CH(Ph)Me)Fe(CO)(L)X. Complexes of this formula exist as mixtures of diastereomerically related pairs of enantiomers, (*RR*), (*SS*) and (*RS*), (*SR*), owing to the presence of an asymmetric CH carbon and an asymmetric iron. In that respect they resemble the previously studied (η^5-C_5H_3-1-Me-3-Ph)Fe(CO)(L)X, which contain an asymmetrically substituted η^5-cyclopentadienyl ring, in addition to an asymmetric metal. Chiral organometallic complexes containing an η^5-C_5H_4CH(Ph)Me ring have been investigated for titanium(IV) [4–6], but, to our knowledge, not for piano-stool iron(II).

Reported here are the synthesis of a number of complexes (η^5-C_5H_4CH(Ph)-Me)Fe(CO)(L)X (L = PPh_3, $PTol_3$, PCy_3, $P(OPh)_3$, $P(OEt)_3$; X = I, Br, Me, COMe, H) and some stereochemical studies of their reactions at chiral iron. We were especially interested in obtaining pure or partly separated diastereomeric pairs of enantiomers of the iron hydrido complexes and in examining stereochemistry at the Fe–H bond.

Experimental

General procedures and measurements

All reactions were carried out under an atmosphere of purified nitrogen. Elemental analysis was done by Galbraith Laboratories, Inc., Knoxville, TN. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin–Elmer Model 283 spectrophotometer or on a Perkin–Elmer Model 1750 Fourier Transform spectrometer calibrated with polystyrene. ^1H NMR spectra were obtained on Varian Associates EM-390L and FT-80A spectrometers. The variable temperature ^1H NMR studies were conducted on Bruker WM-300 and Bruker HX-90 spectrometers. $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker WP-80 spectrometer. In all cases, chemical shifts are reported relative to Me_4Si as an internal reference. $^{31}P\{^1H\}$ NMR spectra were recorded on Bruker HX-90 and Varian Associates FT-80A spectrometers using $(MeO)_3PO$ in a coaxial tube as the reference at +1.59 ppm from 85% H_3PO_4 at 0 ppm. Mass spectra were obtained at 70 eV on an AEI Model MS-9 spectrometer by Mr. C.R. Weisenberger.

Chromatographic separations utilized neutral alumina deactivated with distilled water (6%).

Irradiation experiments were carried out in a Pyrex vessel under a positive nitrogen atmosphere using a Rayonet Model RPR-100 photochemical reactor with sixteen 3500 Å lamps or a 250 W General Electric sunlamp. A Hanovia photochemical apparatus, consisting of a medium-pressure water-jacketed quartz reaction vessel and a 450 W mercury vapor lamp, was used for the preparation of $Fe_2(CO)_9$ according to the procedure of Jolly [7].

Materials

6-Methyl-6-phenylfulvene [8], α-phenethylcyclopentadiene [9], and 1-ethyl-4-phospha-3,5,8-trioxabicyclo[2.2.2]octane (ETPB) [10] were prepared as described in the literature. Iron pentacarbonyl was purchased from Alfa and used directly. Tetrahydrofuran (THF) was purified by distillation from Na and benzophenone immediately before use. Pentane, benzene, and cyclohexane were distilled from sodium. Other solvents were of reagent grade quality and were used as received. Tri-*p*-tolylphosphine, triphenylphosphine, tricyclohexylphosphine, tri-t-butylphosphine, triethylphosphite, and triphenylphosphite were purchased from Strem Chemical Company and used without further purification. The various reducing agents used (K-Selectride, L-Selectride, Super Hydride, $NaBH_4$, and $LiAlH_4$) as well as iodomethane and iodoethane were obtained from Aldrich Chemical Company.

Preparation of $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$

A suspension of 4.5 ml (0.030 mol) of α-phenethylcyclopentadiene and 9.5 g (0.030 mol) of $Fe_2(CO)_9$ in 150 ml of benzene was stirred at room temperature under nitrogen for 24 h. The deep red mixture was filtered, and the filtrate was concentrated under reduced pressure. The resulting red oil was chromatographed on an alumina column prepared with cyclohexane. Elution with cyclohexane afforded a golden band which contained unreacted α-phenethylcyclopentadiene. Subsequent elution with benzene afforded a red band, identified by spectral methods as the desired product. After removal of the solvent, addition of pentane gave 1.35 g (18.0%) of dark red crystals; m.p. 112–115°C dec. Mass spectrum, *m/e* 562 P^+. Anal. Found: C, 64.19; H, 4.84. $C_{30}H_{26}Fe_2O_4$ calc: C, 64.08; H, 4.67%. IR and NMR spectroscopic data for this and other new complexes prepared herein are given in Tables 1 and 2.

Preparation of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2I$

A solution of 2.0 g (3.6 mmol) of $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$ and 1.4 g (5.5 mmol) of iodine in 75 ml of chloroform was refluxed under nitrogen for 1 h. After cooling to room temperature, the black solution was treated with a solution of 10.0 g (40.3 mmol) of $Na_2S_2O_3 \cdot 5H_2O$ in 80 ml of water. The chloroform layer was collected, dried over $MgSO_4$, and filtered. Removal of the solvent from the filtrate gave 2.8 g (95%) of the pure product as a black oil.

Preparation of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Br$

A solution of 0.21 ml (4.1 mmol) of bromine in 50 ml of chloroform was added dropwise over 1 h to a cooled solution of 2.0 g (3.6 mmol) of $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$ in 75 ml of chloroform. The resulting red solution was stirred under nitrogen for 2 h while maintained at 0°C. After warming to room temperature, the reaction solution was extracted with an aqueous sodium thiosulfate solution. The chloroform layer was collected, dried over $CaCl_2$, and filtered. Removal of the solvent gave 2.4 g (92%) of the product as a red oil.

Preparation of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2Cl$

Oxygen was bubbled for 1 h through a solution containing 1.0 g (1.8 mmol) of [(η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2]_2$ in 50 ml of ethanol, 10 ml of chloroform, and 1.5 ml of concentrated hydrochloric acid. After evaporation of the solution to dryness under reduced pressure, the residue was taken up into approximately 100 ml of distilled water. The desired compound was extracted from this solution into 75 ml of chloroform, which was then dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure to afford 0.98 g (86%) of a red oil, identified as the title product by its spectroscopic properties.

Preparation of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2Me$

The salt Na[(η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2$] was prepared by stirring a solution of 2.5 g (4.5 mmol) of [(η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2]_2$ in 80 ml of freshly distilled THF with excess 2% sodium amalgam. The reaction mixture turned from a deep red color to a golden-brown while stirring at room temperature for 1 h under a positive pressure of nitrogen. A solution of 3.0 ml (48 mmol) of MeI in 10 ml of THF was added to the reaction mixture which had been freed of the excess amalgam. After stirring at room temperature for 2 h, the solvent was removed and the residue was extracted into petroleum ether. Filtration through glass filter paper and removal of the solvent gave a golden oil. This oil was dissolved in a minimum amount of chloroform and chromatographed on alumina. Elution with petroleum ether afforded a golden-yellow band of the product. Removal of the solvent from the eluent gave a pure golden oil (2.4 g, 90%) identified as the product through spectral characterization. Elution with chloroform gave a small amount of the dimeric starting material.

Preparation of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$

A solution of 3.0 g (7.4 mmol) of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2I$ and 2.4 g (9.2 mmol) of PPh_3 in 200 ml of benzene was irradiated under nitrogen for 4 h. The resulting green solution was filtered, and the solvent was removed under reduced pressure. The residue was dissolved in a minimum amount of dichloromethane and chromatographed on alumina. Elution with petroleum ether afforded some unreacted triphenylphosphine, and then elution with benzene yielded a green band. The green eluent was collected and concentrated to approximately 10 ml. Pentane was added to yield 3.4 g (72%) of dark green crystals of the product; m.p. 69–72°C. Anal. Found: C, 60.00; H, 4.38. $C_{32}H_{28}FeIOP$ calc: C, 59.83; H, 4.40%.

Preparation of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PTol_3)I$

A solution of 2.2 g (5.4 mmol) of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2I$ and 1.8 g (6.0 mmol) of $PTol_3$ (Tol = *p*-tolyl) in 200 ml of benzene was irradiated for 4 h under a constant stream of nitrogen. The solution was then filtered, concentrated to a small volume, and chromatographed on alumina. Elution with pentane afforded some unreacted tri-*p*-tolylphosphine. Use of 1/1 pentane/benzene afforded a green band which was collected and concentrated to approximately 25 ml. Pentane was added to yield 3.5 g (70%) of green crystals of the desired product; m.p. 70–73°C.

Preparation of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Br$

A solution of 2.6 g (7.2 mmol) of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2Br$ and 2.4 g (9.2 mmol) of PPh_3 in 200 ml of benzene was irradiated under a steady flow of nitrogen for 5 h. The green solution was filtered, reduced in volume to an oil, and chromatographed on alumina. Elution with pentane removed unreacted triphenylphosphine. A large green band was eluted with 1/1 pentane/benzene. Removal of the solvent from this band gave 2.9 g (68%) of green crystalline product, m.p. 90–93°C. Anal. Found: C, 63.87; H, 4.82. $C_{32}H_{28}BrFeOP$ calc: C, 64.56; H, 4.75%.

Preparation of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me)$

A solution of 3.0 g (10.0 mmol) of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Me$ and 2.6 g (10.0 mmol) of PPh_3 in 100 ml of MeCN was maintained at reflux under nitrogen for 14 h. The solvent was removed and the resulting reddish-orange oil was dissolved in a minimum amount of dichloromethane and chromatographed on alumina. Elution with petroleum ether afforded a small yellow band, identified spectroscopically as the starting material. Further elution with 3/1 dichloromethane/benzene afforded an orange band. The eluent was collected and concentrated to approximately 10 ml. Pentane was added to yield 3.6 g (64%) of the orange-red crystals of product. Anal. Found: C, 72.88; H, 5.64. $C_{34}H_{31}FeO_2P$ calc: C, 73.12; H, 5.61%.

Preparation of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me$

A solution of 2.0 g (3.6 mmol) of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me)$ in 150 ml of benzene was irradiated for 4 h. The solution was filtered, concentrated under reduced pressure, and chromatographed on alumina. Elution with petroleum ether afforded a trace yellow band which was identified spectroscopically as $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Me$. Elution with 4/1 pentane/benzene developed an orange/red band, identified as the desired product. Elution with benzene afforded a small purple band, shown by spectral methods to be $[(\eta^5\text{-}C_5H_4CH(Ph)Me)\text{-}Fe(CO)_2]_2$. Using dichloromethane as the eluting solvent gave a golden band of the starting material. The solvent was removed from the orange-red band of the product to give an oil. Addition of pentane afforded 1.1 g (56%) of golden-orange crystals; m.p. 85–87°C (dec.). Anal. Found: C, 73.68; H, 6.02. $C_{33}H_{31}FeOP$ calc: C, 74.72; H, 5.90%.

Preparation of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(L)H$

Method A ($L = PPh_3$, $PTol_3$, PCy_3, $P(OPh)_3$, $P(OEt)_3$, *ETPB*). The title iron hydrido complexes were prepared by a suitable adaptation of the general method of Kalck and Poilblanc for $(\eta^5\text{-}C_5H_5)Fe(CO)(L)H$ [11].

A solution of 1.50 g (3.7 mmol) of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2I$ in 75 ml of anhydrous diethyl ether was added dropwise over 1 h to a cooled suspension of 0.33 g (8.7 mmol) of $LiAlH_4$ in 50 ml of diethyl ether. The resulting brown solution was stirred at room temperature under a positive nitrogen pressure for 1–2 h, after which time an equimolar amount of the phosphine/phosphite ligand was added. The reaction mixture was again stirred at room temperature for at least 1 h while kept under nitrogen. The solution was then cooled, and 30 ml of distilled water was added dropwise to quench the excess $LiAlH_4$. The heterogeneous mixture consisting of a golden-red ether layer and a gray aqueous layer was again left to stir for 1 h under nitrogen. The ether layer was then separated, dried over $MgSO_4$, filtered, and reduced to an oil under vacuum. The oil was loaded onto an alumina/petroleum ether chromatography column using a minimum amount of benzene. Elution with petroleum ether removed any unreacted phosphine/phosphite. Further elution with 4/1 petroleum ether/benzene removed a faint yellow band which could not be identified. A golden-yellow band, identified spectroscopically as the desired product, was eluted with 3/1 petroleum ether/benzene. Removal of solvent gave a golden-yellow oil. Further attempts to purify or crystallize the hydride product were unsuccessful, resulting in extensive decomposition. The yield was 30% (when $L = PPh_3$ or $PTol_3$) or less.

Method B ($L = PPh_3$, $PTol_3$). A solution of 2.0 g (3.1 mmol) of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$ in 100 ml of anhydrous diethyl ether was added dropwise over 1 h to a cooled suspension of 0.40 g (10.5 mmol) of $LiAlH_4$ in 50 ml of diethyl ether under a constant nitrogen atmosphere. The solution was left stirring at room temperature for 1–2 h, after which time it was again cooled in an ice bath and 30 ml of distilled water was added dropwise over 30 min. The ether layer was separated from the water layer, dried over $MgSO_4$, filtered, and reduced to an oil under vacuum. The hydride product was obtained in pure form by chromatography using an alumina/petroleum ether column. After loading with a minimum amount of benzene, elution with 3/1 petroleum ether/benzene removed a golden-yellow band, identified as the product spectroscopically.

Separation of diastereomeric pairs of enantiomers * *of* $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$, $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PTol_3)I$, $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Br$, *and* $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me)$

The crude reaction mixtures from photolysis of the halide complexes were shown by ^1H NMR spectroscopy to contain unreacted phosphine ligand and the two possible diastereomeric products in an approximately 50/50 ratio. In all three cases, column chromatography, as described below, was found to effect a partial separation of these diastereomers. Since the diastereomers were found to be stable on the column, it was possible to carry out repetitive chromatographic separations until an approximately 95/5 ratio of isomers was achieved as determined by ^1H NMR spectroscopy. Additional chromatography or recrystallization did not change this ratio.

Approximately 1.0 g of the green reaction mixture containing the unreacted phosphine ligand and the diastereomeric products was dissolved in an minimum amount of benzene (5 ml) and chromatographed on an alumina column (2 × 25 cm) prepared with petroleum ether. The column was first eluted with petroleum ether to insure complete removal of any unreacted phosphine. When the pale yellow band of the phosphine had been removed, the column was eluted with a 3/1 petroleum ether/benzene mixture. The green product band moved slowly, eventually tailing out across the entire length of the column. This band was collected in approximately 24 fractions of 50 ml each. Analysis of these fractions by ^1H NMR spectroscopy (in C_6D_6) indicated that the first five predominately contained isomer **A** whereas the last five predominately contained isomer **B**. The middle fractions (#6 through #19) were shown to be mixtures of the two isomers and were recombined and rechromatographed. Repetition of this process (on the average four times) made it possible to obtain approximately 0.25 g of each isomer.

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* Also called diastereomers or, simply, isomers in this paper.

The isomerically enriched complexes from chromatography were dissolved in 50 ml of 4/1 pentane/chloroform and stored at 5°C for at least 24 h. The resulting crystals were collected and washed with cold pentane. Approximately 0.18 g of each isomer was obtained. ^{1}H NMR analysis of these crystals showed them to be 95% diastereomerically pure. Further attempts at recrystallization did not improve this isomer ratio and only resulted in decreased yields.

A similar procedure was employed for the separation of the diastereomers of the acetyl complex. Elution was accomplished by using a 2/3 petroleum ether/benzene mixture, which effectively spread the golden-yellow band across the length of the column. Again the front fractions contained an approximately 95/5 ratio of isomers **A**/**B**, and the back fractions were ca. 95/5 **B**/**A**.

Results and discussion

The dimer $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$, which represents the starting material for the synthesis of the chiral complexes described in this paper, was prepared by reaction of α-phenethylcyclopentadiene with $Fe_2(CO)_9$ in benzene at room temperature (eq. 1). It was isolated in 18% yield as a dark red solid; the conversion can be

$$Fe_2(CO)_9 + C_5H_5CH(Ph)Me \rightarrow \left[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2\right]_2 \qquad (1)$$

substantially improved if the recovered α-phenethylcyclopentadiene is used again. The product was characterized by elemental analysis and its IR and ^{1}H and $^{13}C\{^1H\}$ NMR spectroscopic (Tables 1 and 2) and mass spectrometric properties. An attempted synthesis of this complex by treatment of $Fe(CO)_5$ with 6-methyl-6-phenylfulvene [12] in methylcyclohexane at reflux afforded a dark red solid with IR ν(CO) absorptions very similar to those of $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$. However, the product shows a parent molecular ion mass peak at *m/e* 560 (cf. *m/e* 562 for $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$), and its ^{1}H and $^{13}C\{^1H\}$ NMR spectra are incompatible with those of a compound containing $\eta^5\text{-}C_5H_4CH(Ph)Me$. No further attempts were made at characterization of this solid.

The complex $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$ was converted to the mononuclear derivatives $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2X$ (X = I, Br, Cl, Me) by suitable adaptations of the corresponding processes reported for $[(\eta^5\text{-}C_5H_5)Fe(CO)_2]_2$ [13–15] (eq. 2–5). All four products were obtained as oils which could not be induced to crystallize. Their spectroscopic properties, furnished in Tables 1 and 2, are in complete accord with the assigned dicarbonyl structures.

$$\left[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2\right]_2 \xrightarrow{I_2} (\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2I \qquad (2)$$

$$\left[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2\right]_2 \xrightarrow{Br_2} (\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Br \qquad (3)$$

$$\left[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2\right]_2 \xrightarrow[O_2]{HCl,} (\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Cl \qquad (4)$$

$$\left[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2\right]_2 \xrightarrow[(2)\ MeI]{(1)\ Na/Hg} (\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Me \qquad (5)$$

(*Continued on p. 402*)

TABLE 1

IR AND ^{1}H NMR DATA FOR NEW COMPLEXES AT 25°C

Complex	IR ν(CO) (cm^{-1}) [a]	^{1}H NMR δ (ppm) [b]
$[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$	1996, 1953, 1776	7.25 (m, 2Ph), 4.98, 4.36 (br, 2 C_5H_4), 4.14 (q, *J* 7.1 Hz, 2CH), 1.66 (d, *J* 7.1 Hz, 2 Me) [d]
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2I$	2040, 1999	7.25 (m, Ph), 5.13, 4.82 (br, C_5H_4), 3.99 (q, *J* 7.1 Hz, CH), 1.59 (d, *J* 7.1 Hz, Me) [d]
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Br$	2048, 2004	7.27 (m, Ph), 5.15, 4.74 (br, C_5H_4), 3.94 (q, *J* 7.1 Hz, CH), 1.59 (d, *J* 7.1 Hz, Me) [d]
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Cl$	2051, 2007	7.27 (m, Ph), 5.21, 4.76, 4.64 (br, C_5H_4), 3.84 (q, *J* 7.1 Hz, CH), 1.58 (d, *J* 7.1 Hz, Me) [d]
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Me$	2006, 1955	7.22 (m, Ph), 4.73, 4.54, 4.40 (br, C_5H_4), 3.71 (q, *J* 7.2 Hz, CH), 1.51 (d, *J* 7.2 Hz, CH*Me*), 0.14 (s, FeMe) [d]
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$ **A**	1954	7.8–7.0 (m, 4 Ph), 4.94, 4.20, 4.03, 2.77 (br, C_5H_4), 4.45 (q, *J* 7.1 Hz, CH), 1.57 (d, *J* 7.1 Hz, Me)
B	1954	7.8–7.0 (m, 4 Ph), 5.24, 4.60, 3.44, 3.21 (br, C_5H_4), 4.25 (q, *J* 7.1 Hz, CH), 1.61 (d, *J* 7.1 Hz, Me)
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PTol_3)I$ **A**	1951	7.8–6.8 (m, $3C_6H_4$), 7.15 (m, Ph), 5.03, 4.36, 4.10, 2.91 (br, C_5H_4), 4.51 (q, *J* 7.1 Hz, CH), 1.97 (s, 3 CMe), 1.60 (d, *J* 7.1 Hz, CH*Me*)
B	1951	7.8–6.8 (m, $3C_6H_4$), 7.15 (m, Ph), 5.31, 4.73, 3.57, 3.24 (br, C_5H_4), 4.30 (q, *J* 7.1 Hz, CH), 1.97 (s, 3 CMe), 1.64 (d, *J* 7.1 Hz, CH*Me*)
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Br$ **A**	1958	7.8–7.0 (m, 4 Ph), 4.98, 4.23, 2.32 (br, C_5H_4), 4.43 (q, *J* 7.1 Hz, CH), 1.59 (d, *J* 7.1 Hz, Me)
B	1958	7.8–7.0 (m, 4Ph), 5.17, 4.52, 3.30, 2.89 (br, C_5H_4), 4.25 (q, *J* 7.1 Hz, CH), 1.59 (d, *J* 7.1 Hz, Me)

(η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me) **A**	1913, 1590	7.6–7.2 (m, 4 Ph), 4.57, 4.17, 3.99 (br, C_5H_4), 3.85 (q, *J* 7.1 Hz, CH), 2.08 (s, COMe), 1.54 (d, *J* 7.1 Hz, CH*Me*) [d]
B	1911, 1588	7.6–7.2 (m, 4 Ph), 4.69, 4.14 (br, C_5H_4), 3.90 (q, *J* 7.1 Hz, CH), 2.22 (s, COMe), 1.59 (d, *J* 7.1 Hz, CH*Me*) [d]
(η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me **A/B**	1906 [c]	7.7–6.9 (m, 4Ph), 4.5–3.7 (m, C_5H_4, CH), 1.54 (d, *J* 7.3 Hz, CH*Me* **A**), 1.52 (d, *J* 7.3 Hz, CH*Me* **B**), 0.39 (d, *J*(PH) 6.5 Hz, FeMe **A**), 0.28 (d, *J*(PH) 6.5 Hz, FeMe **B**)
(η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H **A/B**	1931 [c]	7.7–7.0 (m, 4 Ph), 4.3–4.0 (m, C_5H_4), 3.77, 3.74 (2q, *J* 7.1 Hz CH), 1.55 (d, *J* 7.1 Hz, Me), −12.66, −12.69 (2d, *J*(PH) 74.5 Hz, FeH)
(η^5-C_5H_4CH(Ph)Me)Fe(CO)($PTol_3$)H **A/B**	1931 [c]	7.8–6.9 (m, 3C_6H_4), 7.15 (m, Ph), 4.4–4.0 (m, C_5H_4), 3.84, 3.80 (2q, *J* 7.1 Hz, CH), 2.01 (s, 3CMe), 1.59 (d, *J* 7.1 Hz, CH*Me*), −12.63, (d, *J*(PH) 74.7 Hz, FeH), −12.67 (d, *J*(PH) 74.6 Hz, FeH)
(η^5-C_5H_4CH(Ph)Me)Fe(CO)(PCy_3)H **A/B**	1902 [c]	7.13 (m, Ph), 4.6–4.3 (m, C_5H_4), 3.95 (q, *J* 7.1 Hz CH), 1.9–1.1 (m, 3Cy, Me), −13.70 (d, *J*(PH) 71.2 Hz, FeH)
(η^5-C_5H_4CH(Ph)Me)Fe(CO)($P(OPh)_3$)H **A/B**	1956 [c]	7.1–6.5 (m, 4 Ph), 3.9–3.5 (m, C_5H_4), 3.14, 3.09 (2q, *J* 7.1 Hz, CH), 1.04, 1.03 (2d, *J* 7.1 Hz, Me), −13.01, −13.03 (2d, *J*(PH) 94.3 Hz, FeH)
(η^5-C_5H_4CH(Ph)Me)Fe(CO)($P(OEt)_3$)H **A/B**	1937 [c]	7.16 (m, Ph), 4.52, 4.34 (br, C_5H_4), 4.2–3.7 (m, CH, CH_2), 1.56 (d, *J* 6.8 Hz, CH*Me*), 1.09 (t, *J* 6.9 Hz, CH_2*Me*), −13.16 (d, *J*(PH) 90.8 Hz, FeH)
(η^5-C_5H_4CH(Ph)Me)Fe(CO)(ETPB)H **A/B**	1956 [c]	7.1 (m, Ph), −14.01 (d, *J*(PH) 115.4 Hz, FeH) [e]

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[a] In $CHCl_3$ unless otherwise noted. [b] In C_6D_6 unless otherwise noted. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. [c] In C_6H_{12}. [d] In $CDCl_3$. [e] Assignments of other signals complicated by decomposition.

TABLE 2

$^{13}C\{^1H\}$ NMR DATA FOR NEW COMPLEXES AT 25°C

Complex	$^{13}C\{^1H\}$ NMR δ (ppm) [a]	$^{31}P\{^1H\}$ NMR δ (ppm) [a]
$[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$	146.30–125.25 (Ph), 111.54, 90.26, 87.85, 86.83, 86.64 (C_6H_4), 37.95 (CH), 22.01 (Me)	
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2I$	213.42, 213.31 (CO), 144.22–127.14 (Ph), 109.60, 85.50, 85.36, 83.53, 79.80 (C_5H_4), 38.23 (CH), 21.64 (Me) [b]	
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Br$	213.68, 213.57 (CO), 144.51–125.25 (Ph), 112.53, 87.15, 86.83, 83.39, 79.92 (C_5H_4), 38.09 (CH), 22.12 (Me)	
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Cl$	212.09 (br, CO), 144.03–127.13 (Ph), 114.73, 85.49, 81.87, 78.12 (C_5H_4), 37.55 (CH), 21.12 (Me) [b]	
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2Me$	218.21, 218.10 (CO), 145.76–126.78 (Ph), 110.04, 85.66, 85.56, 84.38, 81.85 (C_5H_4), 38.39 (CH), 21.97 (CH*Me*), −21.50 (FeMe)	
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$ **A**	228.18 (J(PC) 31.62 Hz, CO), 146.16–126.53 (Ph), 106.15, 91.39, 85.89, 78.25, 73.35 (C_5H_4), 39.09 (CH), 21.39 (Me)	67.17
B	228.18 (J(PC) 31.62 Hz, (CO), 147.19–126.85 (Ph), 106.85, 90.13, 84.53, 81.30, 75.19 (C_5H_4), 39.05 (CH), 22.40 (Me)	68.04
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PTol_3)I$ **A**	[d]	64.55
B	[d]	65.33

$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Br$ **A**	221.49 (J(PC) 31.50 Hz, CO), 147.01–126.54 (Ph), 109.47, 92.65, 86.73, 78.63, 68.08 (C_5H_4), 38.23 (CH), 21.48 (Me)	64.03
B	221.50 (J(PC) 31.50 Hz, CO), 145.67–126.77 (Ph), 109.11, 91.86, 85.45, 75.89, 75.63 (C_5H_4), 38.15 (CH), 22.17 (Me)	64.82
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me)$ **A**	278.68 (br, *C*OMe), 220.82 (J(PC) 30.52 Hz, CO), 146.46–126.39 (Ph), 108.14, 90.30, 88.27, 85.53, 78.57 (C_5H_4), 51.42 (CO*Me*), 38.64 (CH), 22.54 (CH*Me*) [b]	74.67
B	276.57 (br, *C*OMe), 220.98 (J(PC) 30.52 Hz, CO), 146.74–126.35 (Ph), 106.57, 89.25, 88.24, 85.85, 80.35 (C_5H_4), 51.95 (CO*Me*), 38.84 (CH), 22.17 (CH*Me*) [b]	74.50
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me$ **A/B**	224.44 (J(PC) 31.14 Hz, CO), 148.04–127.07 (Ph), 107.22 (J(PC) 3.57 Hz, C_5H_4), 106.45 (J(PC) 2.92 Hz, C_5H_4), 91.62, 90.91, 90.86, 87.08 85.37, 85.02, 81.19, 79.48, 78.49 (C_5H_4), 39.89, 38.97 (CH), 23.10 (CH*Me*), −17.71 (J(PC) 21.63 Hz, FeMe), −18.27 (J(PC) 21.82 Hz, FeMe)	84.25 (**A**), 83.65 (**B**)
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ **A/B**	220.21 (J(PC) 27.36 Hz, CO), 147.16–126.31 (Ph), 108.59, 107.40, 82.58, 80.91, 80.60, 80.13, 79.43, 79.24, 78.26, 77.80 (C_5H_4), 39.64, 39.21 (CH), 22.87, 22.71 (Me)	88.81
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PTol_3)H$ **A/B**	220.48 (J(PC) 27.36 Hz, CO), 147.31–126.27 (Ph, C_6H_4), 108.56, 107.28, 82.70, 81.03, 80.68, 80.13, 79.51, 79.20, 78.23, 77.76 (C_5H_4), 39.75, 39.32 (CH), 22.91, 22.79 (CH*Me*), 21.08 (C*Me*)	86.00
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PCy_3)H$ **A/B**	[d]	93.38, 93.15 [c]
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(P(OPh)_3)H$ **A/B**	[d]	182.61, 182.43 [c]
$(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(P(OEt)_3)H$ **A/B**	[d]	185.36, 185.20

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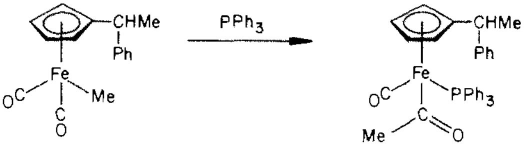
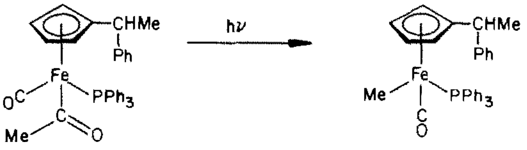
[a] In C_6D_6 unless otherwise noted. [b] In $CDCl_3$. [c] In C_6H_6 with acetone-d_6 lock. [d] Not measured.



(6)

Reaction of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2Me$ with PPh_3 in MeCN at reflux afforded (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me)$ as orange-red, air-stable crystals in 64% yield (eq. 6). The product was obtained as a mixture of diastereomers in roughly equal amounts. This was elucidated by examination of its ^1H NMR spectrum, which showed two resonances for each of the CH, COMe, and CH*Me* protons (Table 1). Separate signals of the two diastereomers were also observed for a number of carbon atoms and for the phosphorus atoms in the respective proton-decoupled NMR spectra (Table 2). The diastereomers were substantially separated by chromatography on alumina as described in the Experimental section. They were designated as **A** and **B** according to the order of elution from the column. Each isomer was obtained in ca. 95% purity as ascertained by integration of the ^1H NMR signals of the COMe protons at δ 2.08 and 2.22.

Photolysis of a 50/50 isomeric mixture of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me)$ in benzene for 4 h afforded the methyl complex (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me$ as golden-orange crystals in 56% yield (eq. 7). As its parent acetyl, the product was obtained as a 50/50 mixture of diastereomers, showing a doubling of the CH*Me* and FeMe ^1H NMR signals (Table 1), as well as of the CH and FeMe $^{13}C\{^1H\}$ NMR signals and the phosphine $^{31}P\{^1H\}$ NMR signals (Table 2). Attempts at separation of these diastereomers by chromatography on alumina, as effected for the precursor acetyl complex, proved unsuccessful. All chromatographic fractions of the broad orange band of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me$ were shown by ^1H NMR spectroscopy to contain a ca. 50/50 mixture of the isomers.

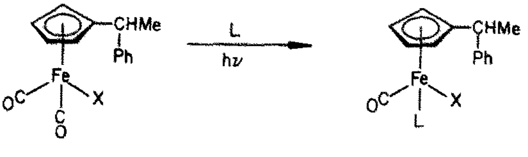


(7)

When the aforementioned photolysis was carried out on a 95/5 **A**/**B** diastereomeric mixture of the acetyl complex under Ar for ca. 40 min, product (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me$ and unreacted (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)(C(O)Me)$ were obtained and separated by chromatography. Integration of the two ^1H NMR signals of the FeMe group revealed that the product consisted of a ca. 65/35 **A**/**B** (arbitrary designation) mixture of diastereomers. The acetyl complex, by contrast, was recovered as an unchanged, 95/5 **A**/**B**, isomeric mixture.

Stereochemistry at metal of the photochemical decarbonylation of chiral iron complexes of the general type (η^5-Ring)Fe(CO)(L)(C(O)R) has been investigated [2,16–18]. Results of those studies point to a highly stereoselective (if not stereospecific) reaction, with inversion at the iron center. However, the reported stereochemistry is complicated to varying degrees by epimerization (or racemization) at metal of the product alkyl complex, which occurs during photolysis. Our present results are entirely compatible with this general picture. Because the product (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)Me was obtained with considerable epimerization at metal, our studies on this system were not pursued further.

Irradiation of (η^5-C_5H_4CH(Ph)Me)Fe$(CO)_2$I and PPh_3 or $PTol_3$, or of (η^5-C_5H_4CH(Ph)Me)Fe$(CO)_2$Br and PPh_3, in benzene for 4–5 h afforded the corresponding monocarbonyl complexes (η^5-C_5H_4CH(Ph)Me)Fe(CO)(L)X as green, air-stable solids in ca. 70% isolated yield (eq. 8). ^{1}H NMR spectra showed that all three

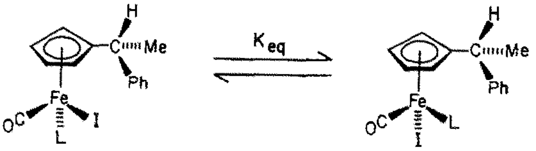


(8)

X = I, L = PPh_3, $PTol_3$; X = Br, L = PPh_3

complexes were obtained as ca. 50/50 mixtures of two diastereomers by the appearance of two resonances for one or both of the CH and CH*Me* groups (Table 1). The presence of two isomers is also apparent in the $^{13}C\{^1H\}$ and/or $^{31}P\{^1H\}$ NMR spectra of these complexes as shown in Table 2. In each case, the diastereomers were separated as highly enriched, 95/5 **A**/**B** and 95/5 **B**/**A**, mixtures by chromatography on alumina. (Again, the designations **A** and **B** refer to the order of elution from the column.) These separations are described in detail in the Experimental section.

Epimerization of the diastereomers **A** and **B** of both (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I and (η^5-C_5H_4CH(Ph)Me)Fe(CO)($PTol_3$)I in C_6D_6 solution was followed by ^{1}H NMR spectroscopy. In each case, the change in intensity of the doublet resonance of the CHMe methyl protons was measured. No change in the spectrum was observed for these complexes in 3 h at 25°C. However, after 30–40 min at 72°C, an approximately 50/50 **A**/**B** mixture was obtained starting with either 95/5 **A**/**B** or 95/5 **B**/**A** of (η^5-C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I. Similarly, both 95/5 **A**/**B** and 95/5 **B**/**A** of (η^5-C_5H_4CH(Ph)Me)Fe(CO)($PTol_3$)I afforded a ca. 50/50 **A**/**B** mixture after 50–55 min at 72°C. Therefore, for each iodo complex, the equilibrium constant, K_{eq} (eq. 9; only one enantiomer of each diastereomer is shown), at 72°C is approximately unity.

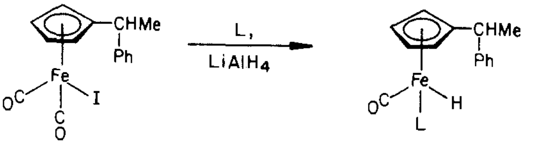


(9)

L = PPh_3, $PTol_3$

Although chiral iron hydrido complexes of the general formula (η^5-C_5H_5)Fe(CO)(L)H have been reported [11,19,20], their enantiomers have not been separated. A principal goal of this investigation was to synthesize chiral iron complexes (η^5-C_5H_4CH(Ph)Me)Fe(CO)(L)H and ascertain whether their diastereomers are stable to epimerization. A successful separation of diastereomers would allow us to conduct stereochemical studies of cleavage reactions of the Fe–H bond.

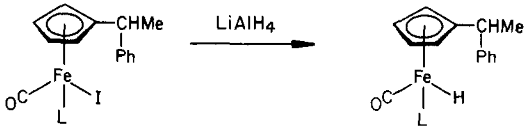
The desired hydrido compounds were prepared by reaction of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2I$ with $LiAlH_4$ in the presence of L (eq. 10), which is an



(10)

L = PPh_3, $PTol_3$, PCy_3, $P(OPh)_3$, $P(OEt)_3$, ETPB

adaptation of the method of Kalck and Poilblanc for (η^5-$C_5H_5)Fe(CO)(L)H$ [11], and by treatment of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(L)I$ with $LiAlH_4$ (eq. 11). They



(11)

L = PPh_3, $PTol_3$

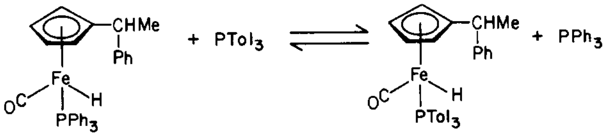
were isolated in ⩽ 30% yield as golden-yellow oils, of which the L = PPh_3 and $PTol_3$ complexes have reasonably good stability in solution, the L = PCy_3, $P(OPh)_3$, and $P(OEt)_3$ complexes are moderately stable in solution, and the L = ETPB complex decomposes readily on chromatography and storage in solution. No reaction was observed for a mixture of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)_2I$, $P(t\text{-}Bu)_3$, and $LiAlH_4$.

The complexes (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(L)H$ with L = PPh_3, $PTol_3$, and $P(OPh)_3$ all exhibit two almost overlapping doublet (J(PH) 74–85 Hz) ^1H NMR resonances for the Fe-H hydrogen at δ −12.6 to −13.1 to indicate the presence of diastereomers. As the temperature of a toluene-d_8 solution of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ was raised, the two doublets remained sharp until ca. 95 °C, when signal broadening owing to considerable decomposition was noted. The other three complexes (L = PCy_3, $P(OEt)_3$, ETPB) each showed a doublet (J(PH) 71–116 Hz, δ −13.1 to −14.0) resonance with somewhat broadened components which could not be resolved into presumed doublets. However, diastereomerism of the L = PCy_3 and $P(OEt)_3$ iron hydrides is revealed by their $^{31}P\{^1H\}$ NMR spectra, each of which consists of two resonances. (A reliable spectrum of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(ETPB)H$ could not be obtained owing to decomposition.) These and other spectroscopic data for the new iron hydrido complexes are set out in Tables 1 and 2.

Chromatography of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ on alumina eluting with 4/1 to 3/1 petroleum ether/benzene developed a broad golden band which was collected in five fractions. To our disappointment, all fractions were shown by ^1H NMR spectroscopy to contain roughly equal amounts of two diastereomers.

Since the diastereomers of (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$ are readily separable and are quite stable toward epimerization (vide supra), we next set out to examine the possibility of synthesizing diastereomeric hydrides (η^5-$C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ by reaction of the separated diastereomers of the corresponding iodo complex with hydride reagents. In that vein, 95/5 **A**/**B** and 95/5 **B**/**A** mixtures of the diastereomers of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$ were treated with $LiAlH_4$ (cf. eq. 11) in diethyl ether or THF as described in the Experimental section. The isolated $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ was shown by ^1H NMR spectroscopy to be a ca. 50/50 mixture of diastereomers. Similar results were obtained by using Super Hydride ($LiBEt_3H$), K-Selectride ($KB(s\text{-}Bu)_3H$), or L-Selectride ($LiB(s\text{-}Bu)_3H$) in THF, except that trace $[(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)_2]_2$ was also isolated and unreacted iodo complex was recovered. No reaction was observed between $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)I$ and $NaBH_4$ in diethyl ether.

The foregoing results prompted us to examine phosphine ligand exchange in $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$, since lability of this ligand could well provide a pathway for epimerization at the iron center. A solution containing $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ and equimolar $PTol_3$ in C_6D_6 at 25°C was monitored by ^1H NMR spectroscopy in the high-field (FeH resonances) region. After about 25 min, the presence of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PTol_3)H$ became readily discernible. The reaction was followed for several hours, as the final ratio of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ to $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PTol_3)H$ remained at ca. 75/25 (eq. 12).



(12)

The substitution of $PTol_3$ for PPh_3 in $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ likely proceeds by the rate-determining dissociation of PPh_3 [21]. This would generate the 16-electron intermediate $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)H$, which may be configurationally unstable *. If the foregoing assumptions are valid, then our inability to separate the diastereomers of $(\eta^5\text{-}C_5H_4CH(Ph)Me)Fe(CO)(PPh_3)H$ probably results from their relatively rapid epimerization via dissociation of PPh_3. The observed rate of the substitution is compatible with this proposal.

Acknowledgements

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* Calculations show that 16-electron systems of the type $(\eta^5\text{-}C_5H_5)Mn(CO)_2$ are pyramidal with a barrier to inversion [22]. However, we expect this barrier to be low when a hydride ligand is present.

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