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THE ADDITION OF HETEROATOMIC NUCLEOPHILES TO DICARBONYL-η^5-CYCLOPENTADIENYL(OLEFIN)IRON CATIONS*

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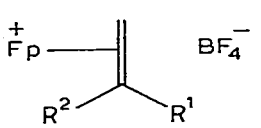
Summary

The additions of a number of heteroatomic nucleophiles, including methanol, amines, phosphines, phosphites and thiols to dicarbonyl-η^5-cyclopentadienyl-(olefin)iron cations are reported. These reactions generally occur with high regiospecificity to monosubstituted olefin complexes, affording a single adduct. The thermal stability of the adducts depends on the nature of the nucleophile and of the olefin substituent. Addition of benzylamine, dimethylamine or trimethylamine to the propene complex takes place competitive with deprotonation of the olefin ligand. Factors affecting the regiospecificity of the reactions are considered.

Introduction

Metal promoted addition of nucleophiles to complexed olefins is a reaction common to a number of transition metal complexes and constitutes a transformation of potential synthetic importance [1]. We recently reported briefly on the addition of several organic and organometallic nucleophiles to dicarbonyl-η^5-cyclopentadienyl(olefin)iron cations (I) [2]. In the present paper we describe the reaction of these complex cations with a number of heteroatomic nucleophiles, among them amines, phosphines, alcohols and mercaptans. (The symbol Fp is used throughout to designate the complex η^5-$C_5H_5Fe(CO)_2$ radical).



(Ia) $R^1 = R^2 = H$
(Ib) $R^1 = Me, R^2 = H$
(Ic) $R^1 = Ph, R^2 = H$
(Id) $R^1 = CHO, R^2 = H$
(Ie) $R^1 = CH_2OMe, R^2 = H$
(If) $R^1 = R^2 = Me$

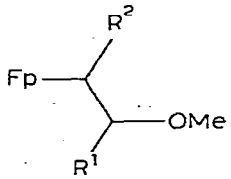
* Taken in part from the Ph.D. Thesis of A. Rosan, Brandeis University, June 1975.

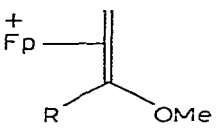
Results and discussion

Alkoxides

The addition of methanol to the cations Ia—Id takes place rapidly at or below room temperature in the presence of sodium carbonate, affording the neutral complexes IIa—IId in moderate to good yields. These substances, the simplest of which has earlier been reported [3] are all exceedingly air sensitive amber oils. Treatment of IIa or IIc with hydride abstractors such as trityl- or triethyl-oxonium tetrafluoroborate led not to the anticipated vinyl ether complexes (IIIa, IIIb) [4], but as with HCl [3] to the starting cations Ia, Ic.

The regiospecificity of the addition reaction of methoxide to Ib—Id appears to be essentially complete. The NMR spectra of the products of these reactions failed to reveal the presence of isomeric adducts. The structures of the adducts IIb and IIc are clearly established by their NMR spectra, which reveal the presence of two diastereotopic protons near τ 8.5 ppm characteristic of the



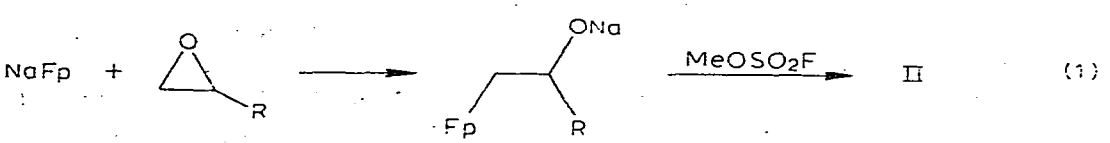


(IIa) $R^1 = R^2 = H$
(IIb) $R^1 = Me, R^2 = H$
(IIc) $R^1 = Ph, R^2 = H$
(IId) $R^1 = H, R^2 = CHO$
(IIe) $R^1 = H, R^2 = Me$

(IIIa) R = H
(IIIb) R = Ph

$FpCH_2$ group. These protons are at τ 8.5 ppm in IIa and at τ 8.4 ppm in $FpCH_2CH_2Ph$ [5]*.

Complexes IIb and IIc were alternatively prepared in low yield by metallation of propylene or styrene epoxide (IVa, IVb) with sodium dicarbonylcyclopentadienylferrate (NaFp), followed by brief treatment of the resulting alkoxide (Va, Vb) with methyl fluorosulfonate (eq. 1).



(IVa) R = Me
(IVb) R = Ph
(IVc) R = CH_2OCH_3

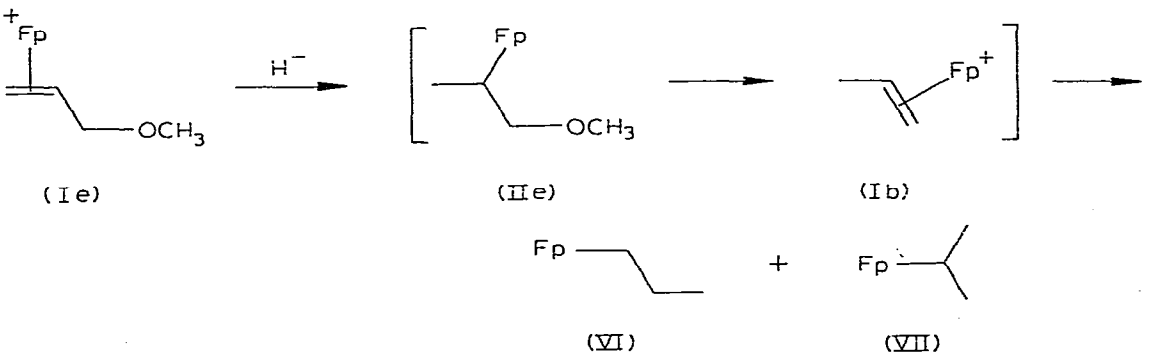
(Va) R = Me
(Vb) R = Ph
(Vc) R = CH_2OCH_3

* This complex may also be prepared by the addition of phenylmagnesium bromide to Ia.

The structure of the adduct IId is evidenced by the low frequency infrared carbonyl absorption at 1629 cm^{-1} typical of α-metallated carbonyl functions [6], and by the appearance of multiplet absorption equivalent to two protons at τ 6.67 ppm. In IIa these α-methoxy methylene protons absorb at τ 6.6 ppm.

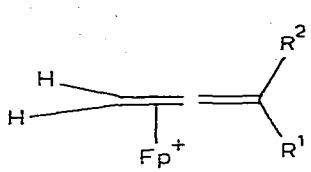
The regiospecificity observed for the reactions of Ib—Id with methoxide closely parallels that observed for the corresponding unsymmetrical bromonium ions with nucleophiles [7], suggesting that the products IIb—IId may be kinetically determined. However thermodynamic product control cannot be excluded, since each of the rea' 'ions examined yields that regioisomer which is most likely the thermodynamically preferred one. Thus, IIb, IIc each have a primary carbon—metal bond [8], while in IId the secondary carbon—metal bond is stabilized by an electron-withdrawing substituent.

In order to examine this point, an attempt was made to examine the stability of the regioisomer IIe which might be formed reversibly in the reaction of Ib with methoxide. The 3-methoxypropene complex Ie was prepared from the reaction of methyl allyl ether epoxide (IVc) with NaFp, followed by protonation of Vc [6c]. On reduction of this cation with sodium borohydride at room temperature, none of the anticipated product IIe was isolated. Instead a mixture of (n-propyl)Fp and (iso-propyl)Fp complexes [6] were obtained. The formation of these latter complexes is readily accounted for by the dissociation of IIe to Ib and its subsequent reduction by excess hydride. The reduction of Ib has previously been reported to yield (iso-propyl)Fp exclusively [9], but a more careful examination of this reaction has now shown that in fact both isomers are formed. Thus, thermodynamic product control in a reversible addition of methoxide to the olefin complexes Ib—Id cannot be excluded.

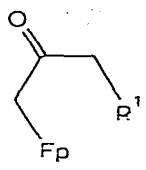


The addition of methoxide in methanol solution to the allene salts VIIIb, VIIId has been reported to give principally the ketones IXb, IXd [10]. We had independently examined the reaction of methoxide with VIIIb and found that when the reagents are carefully dried, the anticipated product Xb may be obtained in 92% yield. However, if the reaction is carried out in 10% aqueous methanol, IXb becomes the major product. It is evidently derived from the addition of water at C(2), which, unlike addition of methanol, would be expected to be irreversible*.

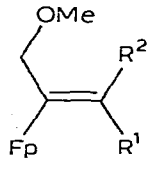
* Lichtenberg and Wojcicki [10] report that treatment of VIIId with hydroxide in aqueous acetone leads to addition at C(1) to give $FpC(CH_2OH)=CHC_6H_5$.



(VIII)



(IX)



(X)

a: $R^1 = R^2 = H$; b: $R^1 = Me, R^2 = H$; c: $R^1 = H, R^2 = Me$; d: $R^1 = Ph, R^2 = H$

The methoxide adduct is formulated as a single geometrical isomer Xb, since it is formed from the *syn*-3-methylalleneiron complex [11], and the stereochemical relationship between the methyl group and the Fp radical in VIIIb would be expected to be preserved in the product. The chemical shift of the vinylic proton in Xb is in accord with this assignment [12]. Treatment of Xb with fluoroboric acid cleanly regenerates the *syn* complex VIIIb.

Amines

The addition of methylamine to Ia has been reported to give an unstable adduct which was incompletely characterized [3]. In our experience, methylamine, either in excess or in 1:1 molar ratio with Ia was found to give a solid product shown to be the 2:1 adduct XIIa. The 1:1 adduct XIa, which must be an intermediate in the formation of XIIa, could not be isolated from the crude reaction product. However, the NMR spectrum of the crude product indicates that XIa is present, but disproportionates on recrystallization to XIIa and methylammonium tetrafluoroborate.

Dimethylamine adds smoothly at —20° C to Ia to give the ammonium salt XIb in moderate yield. The yellow crystalline material is air stable and begins to decompose only at 129° C, before melting with vigorous gas evolution at 137° C. A 2:1 adduct comparable to XIIa was not isolated from this reaction. However, on treatment of XIb with diisopropylamine in the presence of the ethylene complex Ia, further alkylation resulting in the formation of XIIb can be achieved.

Trimethylamine also adds at room temperature to Ia, affording XIc, in good yield, as a yellow air stable solid. The addition is evidently more reversible than for XIb, since brief heating of the salt in THF resulted in its quantitative reversion to Ia.

The reaction of Ia with hydrazine did not give an adduct, but led, as with sodium azide [13], to ligand displacement, affording the known hydrazine complex ($FpNH_2NH_2 \cdot BF_4$) [14] in good yield.

Since tertiary amines are commonly used to deprotonate Fp(olefin) cations possessing allylic protons [15], it was of interest to study the reactions of amines with the propene complex Ib, in order to examine the competition between the addition and deprotonation reactions.

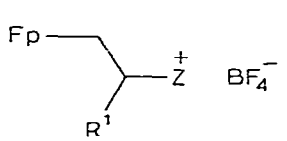
Benzylamine was found to add smoothly to Ib at —25° C, affording the single regioisomeric adduct XId in 89% yield. Its structure is evidenced by the presence of two one-proton signals in the NMR spectrum at τ 9.01 and 8.11 ppm,

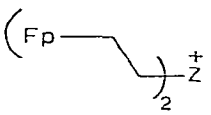
assignable to diastereotopic $FpCH_2$ protons, and a one-proton signal at τ 6.55 ppm characteristic of the Me_3N^+CH grouping.

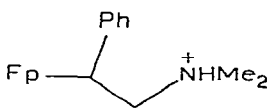
Dimethylamine likewise adds rapidly and regiospecifically at 0°C to give the ammonium salt XIe in essentially quantitative yield. The NMR spectrum of the adduct exhibits two high field one-proton resonances at τ 8.25 and 8.90 ppm and a one-proton multiplet at τ 6.5 ppm, consistent with this structural assignment.

Addition of trimethylamine to Ib takes place at —30°C and affords the salt XIf in 69% yield. Consistent with its structural assignment the NMR spectrum exhibited one-proton signals at τ 6.5, 7.95 and 9.05 ppm for $R_3\overset{+}{N}CH$ and $FpCH_2$ protons. This adduct is significantly less stable than the quaternary ammonium salt derived from Ia. Above —10°C the salt undergoes reversion to Ib and trimethylamine, followed by slower but irreversible conversion to (η^1-allyl)-Fp and trimethylammonium tetrafluoroborate.

In sharp contrast to the regiospecificity exhibited by amines with the propene salt Ib, the styrene salt Ic reacts with dimethylamine to give a single regioisomer in 91% yield, which is shown to have structure XIII. This is clearly evidenced by the absence of high field proton resonance typical of the $FpCH_2$ methylene protons. Instead CH_2 and CH protons constitute an *ABX* set of signals between τ 5.8 and 6.7 ppm.







(XIII)

(XIa) R^1 = H, Z = NH_2Me
(XIb) R^1 = H, Z = $NHMe_2$
(XIc) R^1 = H, Z = NMe_3
(XId) R^1 = Me, Z = NH_2CH_2Ph
(XIe) R^1 = Me, Z = $NHMe_2$
(XIf) R^1 = Me, Z = NMe_3

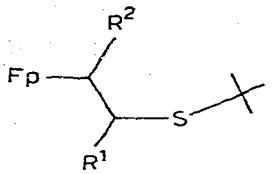
(XIIa) Z = NHMe
(XIIb) Z = NMe_2

Mercaptans

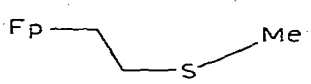
Addition of t-butyl mercaptan to Ia occurred smoothly at 0°C in acetonitrile solution in the presence of K_2CO_3 with the formation of the adduct XIVa in high yield. The addition of mercaptan takes place more slowly than does methanol and the adduct is more stable. Thus, in contrast to IIa, XIVa could be chromatographed on deactivated neutral alumina. The material is a yellow-green solid m.p. 55.5—56.6°C, which was readily characterized by analytical as well as spectral data. In contrast to XV, which has been prepared by metallation of 2-chloroethyl methyl sulfide [16] and is reported to exhibit only two A_2M_2 triplet signals for the methylene protons, XIVa shows complex $AA'BB'$ multiplet resonances for these protons. The adduct XIVa reacts with trityl cation at 0°C, regenerating the ethylene complex in high yield.

When t-butyl mercaptan is added to the propylene complex Ib, two regioisomers are formed in high yield in a ratio of approximately 1.5:1, as is evidenced by the appearance of two cyclopentadienyl proton resonances. These

isomers, formulated as XIVb and XIVc, could not be separated chromatographically but were characterized together by their spectral and analytical data.



(XIVa) $R^1 = R^2 = H$
(XIVb) $R^1 = Me, R^2 = H$
(XIVc) $R^1 = H, R^2 = Me$
(XIVd) $R^1 = H, R^2 = Ph$



(XV)

The low regiospecificity of this reaction stands in sharp contrast to the addition of methanol or amines to Ib. There would appear to be an increased preference for attack by the sulfur nucleophile at the less highly alkylated center of the cation Ib. With the styrene complex Ic, the preference for nucleophilic attack at the primary center is complete and the sole product of the reaction, isolated in 86% yield, is XIVd. The result, however, parallels the reaction of this cation with dimethylamine.

Phosphines

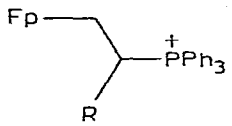
The reaction of triphenylphosphine with Ia takes place rapidly at room temperature and leads to the quantitative formation of the adduct phosphonium salt XVIa. The adduct is a brilliant yellow, air stable, crystalline material, which was fully characterized by spectroscopic and analytical data. An attempt to cleave the iron—carbon bond in XVIa by treatment with HCl in refluxing chloroform, conditions normally effective for such a transformation [17,6b] led to its recovery unchanged. Similarly, attempted reduction [18] with lithium aluminum hydride in refluxing ether was without effect. However, decomposition of the adduct to the phosphonium salt XVII and ethylene was found to occur on heating a suspension in tetrahydrofuran.

In contrast to the stability of XVIa, the adduct derived from the propylene cation Ib and triphenylphosphine is relatively unstable. At temperatures between —10 and 25°C addition of triphenylphosphine to Ib competes with displacement of the olefin ligand to give the phosphonium salt XVII. The reversion of the adduct to XVII and free propylene can be observed to occur rapidly at 65°C in nitromethane in the NMR probe, and brief refluxing of the adduct in this solvent led to a quantitative recovery of XVII. Addition of triphenylphosphine to Ib appears to occur regiospecifically since only a single cyclopentadienyl proton resonance is observed at τ 4.90 ppm. The adduct is formulated as XVIb, on the basis of the presence of a broad one-proton multiplet at τ 6.3 ppm in its spectrum, which may be assigned to the methine proton [19]. Consistent with this structure the methyl proton signal in XVIb is a double doublet (J 7, 21 Hz)*.

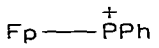
No adduct could be isolated from the reaction of the styrene cation Ic with

* The methyl proton signal for triphenylisopropylphosphonium iodide is a double doublet (J 7, 18.5 Hz), while that for triphenylisobutylphosphonium iodide shows no coupling to phosphorus [19].

triphenylphosphine. However the formation and rapid decomposition of an adduct can be observed in the NMR probe. The addition is regiospecific, as judged by the appearance of a single cyclopentadienyl proton resonance at τ 5.00 ppm. The adduct is tentatively assigned as XVIc assuming thermodynamic product control.



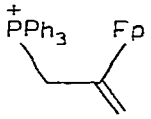
(XVIa) R = H
(XVIb) R = Me
(XVIc) R = Ph



(XVII)

The addition of an equivalent of triphenylphosphine at room temperature to nitromethane solutions of Fp(olefin)$^+$ cations derived from isobutylene, acrolein, cyclopentene, cyclohexene, 1,5-cyclooctadiene (mono-coordinated) and *trans*-2-butene resulted in the quantitative formation of XVII. No evidence for the transient formation of an adduct could be obtained.

By contrast, reaction of the allene cation VIIIa with triphenylphosphine at 0° C gave a quantitative yield of the adduct XVIII. This substance, like that reported earlier with XVIIIb [10] is exceedingly stable. The complex melts with decomposition at 95° C, but nitromethane solutions could be heated to 100° C for one hour without either detectable reversion to starting materials or transformation to XVII. The difference in thermal stability between these adducts

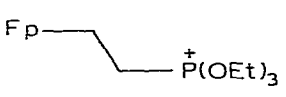


(XVIII)

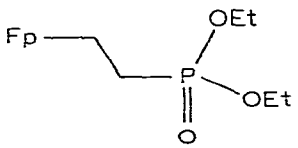
and those derived from simple olefins may reflect the larger bond energy associated with a vinyl—iron bond [20,21].

Phosphites

Despite the reduced basicity of phosphites compared with phosphines, triethyl phosphite was found to add to Ia to give a quantitative yield of the adduct XIX. This material was converted, without purification to the phosphonate ester XX, by treatment with LiCl in dimethyl sulfoxide [22], The phosphonate complex is an air stable orange oil, which was characterized by spectral and analytical data.



(XIX)



(XX)

Regiospecificity of nucleophilic additions. General considerations

In many respects, the direction of nucleophile addition to unsymmetrical Fp(olefin) cations resembles that of epoxide ring opening in acid media [23] or of bromonium ion reactions [7] with nucleophiles. However, steric factors, which appear to play a more important role in epoxide ring opening than in bromonium ion reactions, may be a still more significant component in the reactions of Fp(olefin) cations. Bond making may therefore be more advanced than bond breaking for the reactions of the complex cations compared with either of the former reactions. Such factors may account for the low regiospecificity of the reaction of t-butyl mercaptan with Ib and for attack of sulfur and amine nucleophiles at the primary carbon atom in the styrene complex Ic. A further feature of these reactions, clearly manifest with triphenylphosphine and inferentially with methanol, is their reversibility. Consequently thermodynamic product control rather than kinetic control cannot be ruled out for some of the addition reactions observed. It seems therefore that resolution of these problems must await kinetic measurements and experiments designed to separate steric, inductive and resonance effects.

Experimental

Solvents were routinely dried by standard procedures, maintained under nitrogen over molecular sieves, and degassed prior to use.

All reactions, subsequent purification procedures, and spectroscopic examinations were performed under nitrogen. Reactions were conducted in flame dried apparatus.

Infrared spectra were recorded on Perkin—Elmer model 137 and 457 spectrophotometers. Nuclear Magnetic Resonance spectra were recorded on Varian Model A 60-A (NIH GM-13183), Perkin—Elmer R-32 (NSF GU-3852), and Bruker WH-90 (NSF GU-3852, GP-37156) spectrometers.

Melting points were determined in sealed capillaries and are uncorrected.

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee.

Preparation of 1-Fp-2-methoxyethane (IIa)

A suspension of Fp(ethylene)BF_4 (0.584 g, 2.0 mmol) in 25 ml of methanol was treated with Na_2CO_3 (0.265 g, 2.5 mmol) at room temperature. The starting organometallic salt totally dissolved within a few minutes and the resulting reaction mixture was stirred for 1 hour. The mixture was filtered, evaporated, and the Skelly-B soluble portion of the residue cooled to —78°C whereupon a yellow crystalline material separated. This was quickly filtered and washed with cold Skelly-B to give 0.378 g of product as yellow crystals, (80%) m.p. 0°C: IR (KBr) 2005, 1940 cm^{-1}, NMR (CS_2) τ (ppm) 5.18 (s, 5, Cp), 6.74 (s, 3, OCH_3), 6.6 (m, 2, $C\underline{H}_2OCH_3$) 8.5 (m, 2, $C\underline{H}_2Fp$)*.

Complex IIa (0.178 g, 0.75 mmol) in 1 ml CH_2Cl_2 was treated with a solution of trityl BF_4 (0.265 g, 0.80 mmol) in 2 ml CH_2Cl_2 at 0°C. A precipitate

* The sensitivity of this and other methanol adducts precluded analysis.

formed immediately and after 15 minutes the product was isolated by addition of the reaction mixture to cold Et_2O. A yellow solid was collected by filtration and identified as Fp(ethylene)BF_4 (100 mg, 46%) by comparison of the IR and NMR spectra with those of an authentic sample.

Similarly IIa (0.189 g, 0.80 mmol) in 0.5 ml CH_2Cl_2 was treated with a CH_2Cl_2 solution of Et_3OBF_4 (0.68 ml of 1.26 *M* solution) at 0°C. After a few minutes a solid began to separate out of solution and after 15 minutes the reaction mixture was added to excess Et_2O at 0°C. The product was collected by filtration to provide 0.191 g (83%) of Ia.

Preparation of 1-Fp-2-methoxy propane (IIb)

A suspension of Fp(propene)BF_4 (0.612 g, 2.0 mmol) in 25 ml of methanol was treated with Na_2CO_3 (0.265 g, 2.5 mmol) at room temperature. The organometallic salt totally dissolved within a few minutes and the resulting reaction mixture was stirred for 1 hour. The mixture was then filtered, evaporated, and the residue was purified by sublimation at room temperature (0.05 mmHg) to give a waxy yellow solid. This material melts to an air-sensitive amber liquid below room temperature. The yield was 0.385 g, (77%); IR (film) 2002, 1942 cm^{-1}; NMR (CS_2) τ (ppm) 5.30 (s, 5, Cp), 6.84 (s, 3, OCH_3), 6.92 (m, 1, C<u>H</u>(OCH_3)), 8.54 (m, 2, diastereotopic CH_2Fp), 8.89 (d, 3, CH_3, *J* 6.0 Hz).

Anal. found: C, 52.32, 52.76, 53.25; H, 5.18, 5.40, 5.53. $C_{11}H_{14}FeO_3$ calcd.: C, 52.86; H, 5.64%.

Preparation of 1-Fp-2-methoxy-2-phenylethane (IIc)

A solution of Fp(styrene)BF_4 (0.368 g, 1.0 mmol) in 25 ml of methanol was treated with Na_2CO_3 (0.159 g, 1.5 mmol) at room temperature. The reaction mixture was stirred for 30 minutes, then filtered, evaporated, and the residue taken up in Skelly-B. This solution was filtered and the residual oil was chromatographed on 15 g of activity III neutral alumina. Elution with 1:1 Et_2O/hexane gave a yellow band which yielded an air sensitive amber liquid, 0.055 g (18%); IR (film) 2004, 1942 cm^{-1}; NMR (CS_2) τ (ppm) 2.64 (s, 5, phenyl), 5.25 (s, 5, Cp), 6.00 (dd, 1, C<u>H</u>(phenyl)(OCH_3), *J* 8.5, 4.0 Hz), 6.85 (s, 3, OCH_3), 8.33 (3 lines, 2, diastereotopic CH_2Fp).

Reaction of IIc with trityl hexafluorophosphate

A solution of 1-Fp-2-methoxy-2-phenylethane (0.055 g, 0.176 mmol) in 0.50 ml CH_2Cl_2 was treated dropwise with a solution of tritylPF_6 (0.076 g, 0.180 mmol) in 0.75 ml CH_2Cl_2 at 0°C. An immediate reaction occurred as evidenced by precipitation of a solid. After 15 minutes the product was isolated by addition of the reaction mixture to an excess of dry ether at 0°C. The yellow solid was collected and shown to be Fp(styrene)PF_6 (0.041 g, 63%), by comparison of the IR and NMR spectra with those of an authentic sample.

Preparation of 3-Fp-2-methoxypropionaldehyde (IId)

A suspension of Fp(acrolein)BF_4 (0.321 g, 1.0 mmol) in 10 ml of methanol was treated with Na_2CO_3 (0.159 g, 1.5 mmol) at 0°C. The resulting reaction mixture was stirred for 1 hour during which time the color gradually changed

from orange to deep red. The mixture was filtered and the filtrate evaporated to leave an amber oil which was taken up in ether, filtered through a small plug of $MgSO_4$ and evaporated to give IId as an air sensitive amber liquid, 0.110 g (41%); IR (film) 2010, 1957, 1629 cm^{-1}; NMR (CS_2) τ (ppm) 0.71 (d, 1, C<u>H</u>O, J 4.5 Hz), 5.19 (s, 5, Cp), 6.67 (m, 2, diastereotopic C<u>H</u>$_2$OMe), 6.78 (s, 3, OCH_3), 7.42 (ddd, 1, FpC<u>H</u>, J 10.5, 4.5, 4.5 Hz).

Reaction of cation Ie with sodium borohydride

A suspension of Fp(allyl methyl ether)BF_4 (Ie) (0.336 g, 1.0 mmol) in 5 ml of THF was treated with $NaBH_4$ (0.038 g, 1.0 mmol) in small portions at —25° C. The resulting reaction mixture was stirred at —25° C for 15 minutes whereupon it darkened considerably. Stirring was continued for an additional hour at 0° C. The mixture was filtered through a small plug of activity III basic alumina, washed with hexane and the filtrate evaporated. The residue consisted of an amber oil and the dimer, Fp_2. The hexane-soluble portion of this residue was sublimed at room temperature (0.05 mmHg) and the sublimate was collected on a cold finger cooled to —78° C. This material, 0.050 g (23%), was shown to consist of a mixture of the Fp(isopropyl) and Fp(n-propyl) complexes (ratio 2:1) by comparison of the NMR spectra with those of authentic samples. A small amount of ferrocene and Fp(η^1-cyclopentadiene) complex was also isolated.

Preparation of IIb from propylene oxide

To a solution of NaFp (20.0 ml, 0.5 *M* THF, 10.0 mmol) at 0° C was added propylene oxide (0.70 ml, 10.0 mmol). The resulting solution was stirred for 30 minutes at 0° C whereupon the color changed from orange to green. Methyl fluorosulfonate (0.81 ml, 10.0 mmol) was added, and the ice bath was removed. Stirring was continued for an additional hour at room temperature. Solvent was removed and the residue was extracted with 400 ml of petroleum ether (20/40). The extracts were filtered through sand followed by filtration through activity III basic alumina. The yellow filtrate was stripped. The residue consisted of IIb along with ferrocene, $FpCH_3$ and Fp(η^1-C_5H_5).

Preparation of IIc from styrene oxide

To a solution of NaFp (16.0 ml, 0.25 *M* THF, 4.0 mmol) at 0° C was added styrene oxide (0.50 ml, 4.35 mmol). The resulting solution was stirred for 30 minutes at 0° C whereupon the color had changed from orange to green. Methyl fluorosulfonate (0.30 ml, 3.75 mmol) was added, and stirring was continued for 5 minutes. Solvent was removed and the residue was extracted with 200 ml of petroleum ether. The extracts were filtered through activity III basic alumina and the yellow filtrate was stripped. The residue consisted of a small amount of IIc along with ferrocene and Fp(η^1-C_5H_5).

Failure of IIb to react with $NaBH_4$

Fp(propene)BF_4 (0.612 g, 2.0 mmol) was partially dissolved in 10 ml of methanol at 0° C and sodium carbonate (0.212 g, 2.0 mmol) was added. The resulting reaction mixture was stirred at 0° C for 30 minutes and then filtered through a small plug of Celite. The solvent was removed and the amber oil obtained (IIb, 0.250 g) was dissolved in 5 ml of THF at —78° C and $NaBH_4$

(0.080 g, 2.0 mmol) was added in small portions. The resulting mixture was warmed slowly to 0°C, solvent was then removed, and the resulting semisolid residue was extracted with petroleum ether (20/40). This solution was filtered and evaporated leaving an amber liquid, 0.200 g (80%) identified by NMR as pure IIb. Complexes VI and VII were not detected.

Preparation of Fp(n-propyl) and Fp(iso-propyl) (VI and VII)

Fp(propene)BF_4 (0.918 g, 3.0 mmol) suspended in 15 ml of dry THF at —78°C was treated with $NaBH_4$ (0.125 g, 3.3 mol) in small portions. The reaction mixture was warmed slowly to —10°C over 2 hours. The mixture was stripped at 0°C and the residue was chromatographed on 15 g activity III neutral alumina. Elution with petroleum ether (20/40) provided 0.480 g (73%) of an amber oil shown by NMR to consist of a 3:1 mixture of VI and VII.

Preparation of complex Xb

Fp(*syn*-3-methylallene)BF_4 (VIIIb) (0.318 g, 1.0 mmol) was dissolved in 10 ml of anhydrous methanol at 0°C, and 0.159 g (1.5 mmol) of Na_2CO_3 was added. After stirring at 0°C for 30 min, the mixture was filtered, stripped, and the residue extracted with hexane. Removal of solvent left 0.240 g of Xb as an amber liquid (92%); IR (neat) 2010, 1949 cm^{-1}; NMR (CS_2) τ (ppm) 3.82 (q, 1, *J* 6.5 Hz, CH=), 5.22 (s, 5, Cp), 6.22 (m, 2, CH_2O), 6.82 (s, 3, CH_3O), 8.27 (dm, 3, *J* 6.5 Hz, CH_3).

Anal. found: C, 55.10, 54.98; H, 5.32, 5.22. $C_{12}H_{14}FeO_3$ calcd.: C, 55.00; H, 5.39%.

Reversion of complex Xb in the presence of acid

Complex Xb (0.030 g, 0.12 mmol), dissolved in 5 ml of anhydrous ether at 0°C was treated with HBF_4 etherate (0.12 mmol). The precipitate which formed immediately was collected and identified as VIIIb (0.035 g, 96%) on the basis of IR and NMR spectral data.

Preparation of complex IXb by hydration of VIIIb, VIIIc

An equilibrium mixture of VIIIb/VIIIc (1:2) (0.240 g, 0.75 mmol) [11] was dissolved in 10 ml of 10% aqueous methanol at 0°C, and 0.106 g (1.0 mmol) of Na_2CO_3 was added. The resulting solution was stirred at 0°C for 1 hour, and then poured into 25 ml of water. After extraction with ether, workup gave 0.150 g of product which was shown by an NMR spectrum to be a mixture of IXb [10], Xb and Xc (2:0.5:0.5, respectively).

Addition of methylamine to Ia. Preparation of XIIa

Excess methylamine was bubbled into a solution of Ia (3.2 g, 11 mmol) in 30 ml of acetonitrile at room temperature. The resulting solution was transferred under nitrogen to 750 ml of ether. The yellow precipitate was filtered off and the mother liquor was concentrated and then diluted with ether to yield a second crop of product. This material appears to be a mixture of XIIa, XIa, and methylammonium tetrafluoroborate. Attempts to isolate XIa from this mixture by successive recrystallization from methylene chloride or nitromethane led to apparent disproportionation and the isolation of methylammonium tetrafluoro-

borate and impure XIIa. The NMR spectra also showed the presence of Ia in these mixtures. The filtrate from the second precipitate was evaporated to dryness, washed several times with ether and recrystallized from methylene chloride to yield XIIa as a yellow solid; IR (KBr) 1998, 1932 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 8.70 (m, 4, $FpCH_2$), 7.13 (s, 3, NCH_3), 6.71 (m, 4, NCH_2), 5.00 (s, 10, Cp).

Anal. found: C, 43.43; H, 4.07; N, 2.48. $C_{19}H_{22}BF_4Fe_2NO_4$ calcd.: C, 43.31; H, 4.21; N, 2.66%.

Preparation of (2-Fp-ethyl)dimethylammonium tetrafluoroborate (XIb)

Dimethylamine (3.8 mmol) was condensed at —196°C on a vacuum line into a flask containing 0.500 g (1.71 mmol) of Ia dissolved in 30 ml of degassed acetonitrile. The mixture was warmed to —20°C and stirred at this temperature for 1.5 h. Solvent was removed in vacuo and the solid residue was washed with ether and recrystallized from methylene chloride to give 0.277 g (48%) of XIb as yellow crystals, dec. 129°C; IR (KBr) 2008, 1946 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 5.00 (s, 5, Cp), 6.73 (m, 2, NCH_2), 7.10 (s, 6, CH_3); 8.70 (m, 2, $FpCH_2$).

Anal. found: C, 38.83; H, 4.70; N, 4.05. $C_{11}H_{16}BF_4FeNO_2$ calcd.: C, 39.22; H, 4.79; N, 4.16%.

Preparation of bis(2-Fp-ethyl)dimethylammonium tetrafluoroborate (XIIb)

The ammonium salt XIb (329 mg, 1 mmol) was taken up in 5 ml of acetonitrile, and 321 mg (1.1 mmol) of cation Ia and 130 mg (1 mmol) of diisopropylethylamine was added to this at 0°C. After 30 min 25 ml of ether was added and the yellow precipitate was collected, and recrystallized several times from CH_2Cl_2/ether solutions to give 265 mg of XIIb as yellow crystals, m.p. 142—143°C (dec.); IR (KBr) 2010, 1950 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 4.96 (s, 10, Cp), 6.6 (m, 4, $C\underline{H}_2\overset{+}{N}Me_2$), 7.05 (s, 6, $\overset{+}{N}CH_3$), 8.65 (m, 4, $FpCH_2$).

Anal. found: C, 49.13; H, 5.05; N, 3.17. $C_{20}H_{24}BF_4FeNO_4$ calcd.: C, 49.51; H, 4.95; N, 2.88%.

Preparation of (2-Fp-ethyl)trimethylammonium tetrafluoroborate (XIc)

Excess trimethylamine was bubbled into a solution of Ia (0.59 g, 2.0 mmol) in acetonitrile at room temperature, over a period of 30 min. Solvent was removed in vacuo and the crude product was recrystallized from methylene chloride/ether, to give 0.51 g of XIc (73%) as a yellow powder, dec. 122°C; IR (KBr) 2004, 1934 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 4.97 (s, 5, Cp), 6.57 (m, 2, CH_2N), 6.95 (s, 9, CH_3), 8.65 (m, 2, $FpCH_2$).

Anal. found: C, 40.27; H, 5.15; N, 3.62. $C_{12}H_{18}BF_4FeNO_2$ calcd.: C, 41.07; H, 5.17; N, 3.99%.

Decomposition of XIc

The salt XIc was heated briefly at reflux in THF solution. The product isolated by removal of solvent was shown by NMR and IR spectra to be almost pure Ia with a trace of XIc.

Addition of benzylamine to Ib. Preparation of XId

A solution of 0.298 g (0.98 mmol) of Ib in 1.5 ml of nitromethane and 4 ml of methylene chloride was stirred at —60°C while 0.119 g (1.11 mmol) of

benzylamine was added. The temperature was allowed to rise to —25° C over 15 min. The product was then precipitated by the addition of 24 ml of Skelly-B. This was collected and dried in vacuo at 0° C to give 0.358 g (89%) of XIII as a yellow powder which was analyzed without further purification; IR (KBr) 2001, 1950 cm^{-1}; NMR τ (ppm) 2.54 (s(br), 5, Ph), 3.88 (s(br), 2, NH_2), 5.03 (s, 5, Cp), 5.67 (s, 2, $PhCH_2$), 6.55 (m, 1, CHN), 8.47 (d, 3, J 6.5 Hz, CH_3), 8.11 and 9.01 (m, 2, diastereotopic $FpCH_2$).

Anal. found: C, 49.25; H, 4.80; N, 3.41. $C_{17}H_{20}BF_4FeNO_2$ calcd.: C, 49.44; H, 4.88; N, 3.39%.

Preparation of (1-Fp-isopropyl)dimethylammonium tetrafluoroborate (XIe)

Dimethylamine was bubbled into a solution of 918 mg (3 mmol) of the propylene salt (Ib) in 20 ml of acetonitrile cooled to —30°C. The solution was allowed to warm to 0° C and 65 ml of ether was added. The yellow precipitate was collected and recrystallized from CH_2Cl_2/ether to give 990 mg (96%) of XIe as yellow crystals, dec. 125° C; IR (KBr) 2004, 1945 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 4.96 (s, 5, Cp), 6.5 (m, 1, CHNMe), 7.1 (s, 6, NCH_3), 8.25 (m, 1, $FpCH_2$) 8.55 (d, 3, J 7 Hz, CCH_3), 8.9 (dd, 1, J 10,12 Hz, $FpCH_2$).

Anal. found: C, 40.98; H, 5.19; N, 3.92. $C_{12}H_{18}BF_4FeNO_2$ calcd.: C, 41.02; H, 5.16; N, 3.98%.

Preparation of (1-Fp-isopropyl)trimethylammonium tetrafluoroborate (XIf)

Trimethylamine was bubbled into a solution of Ib (612 mg, 2 mmol) in 10 ml of acetonitrile cooled to —30° C. After 20 min the solution was allowed to warm to —20° C and 45 ml of cold ether was added. After 10 min the product was collected and recrystallized from cold methylene chloride/ether (—20° C) to give 504 mg (69%) of salt (XIf) as a yellow solid, dec. 94°C; IR (nujol) 2008, 1947 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 4.9 (s, 5, Cp), 6.5 (m, 1, CHNMe), 6.9 (s, 9, $N(CH_3)_3$), 7.95 (m, 1, $FpCH_2$), 8.45 (d, 3, J 8 Hz, CCH_3), 9.05 (m, 1, $FpCH_2$).

Anal. found: C, 40.65; H, 5.38; N, 3.54. $C_{13}H_{20}BF_4FeNO_2$ cacld.: C, 42.76; H, 5.55; N, 3.84%.

Thermolysis of XIf

A solution of XIf in deuterionitromethane in an NMR tube was allowed to warm to 15° C in the NMR probe while decomposition was followed. After 20 min decomposition was complete as evidenced by the complete disappearance of the cyclopentadienyl peak at τ 4.9 ppm and the appearance of a new one at τ 5.1 ppm. The solution was then filtered through a small amount of celite, washed with petroleum ether (20/40) and an NMR spectrum of the product was taken which showed it to be identical with (η^1-allyl)Fp.

Preparation of (2-phenyl-2-Fp-ethyl)dimethylammonium tetrafluoroborate (XIII)

Dimethylamine was bubbled into a solution of Ic (740 mg, 2 mmol) in 10 ml of acetonitrile cooled to —30° C. After 15 min the solution was warmed to 0° C and the product was precipitated by the addition of 55 ml of ether. The product was collected and recrystallized from methylene chloride/ether to give 745 mg (91%) of the ammonium salt XIII as yellow crystals, m.p. 109—110° C

(dec.); IR (KBr) 2010, 1940 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 2.75 (m, 5, Ph), 5.08 (s, 5, Cp), 5.9 (dd, 1, *J* 12, 13 Hz, NCH_2), 6.1 (dd, 1, *J* 13,3 Hz, NCH_2), 6.6 (dd, 1, *J* 12, 3 Hz, FpCH), 7.3 (s, 6, NCH_3).

Anal. found: C, 49.23; H, 5.05; N, 3.17. $C_{17}H_{20}BF_4FeNO_2$ calcd.: C, 49.44; H, 4.88; N, 3.39%.

Preparation of Fp(hydrazinium)BF_4

A suspension of Fp(ethylene)BF_4 (0.438 g, 1.5 mmol) in 50 ml of methylene chloride was treated with 95% hydrazine (0.48 ml, 1.5 mmol) at −30°C. The solution was allowed to come to room temperature and the pale yellow solid (0.330 g, 74%) was collected and identified as the title complex by comparison of IR and NMR spectra with published data [14].

Preparation of t-butylthio-2-Fp-ethane (XIVa)

To a suspension of Fp(ethylene)BF_4 (0.584 g, 2.0 mmol) and K_2CO_3 (0.276 g, 2.0 mmol) in 10 ml of CH_3CN at 0°C was added t-butyl mercaptan (0.22 ml, 2.0 mmol). The resulting reaction mixture was stirred at room temperature for 4 hours, then filtered and stripped. The residue was chromatographed on 25 g of activity III neutral alumina. Elution with Et_2O gave the product as a yellow orange liquid which solidified on cooling (0.480 g, 82%). The analytical sample was recrystallized from petroleum ether (20/40), m.p. 55.5—56.5°C; IR (KBr) 2012, 1988, 1942, 1905 cm^{-1}, (CH_3CN) 2012, 1949 cm^{-1}, (petroleum ether) 2024, 1934 cm^{-1}, (film) 2008, 1957 cm^{-1}; NMR (CS_2) τ (ppm) 5.32 (s, 5, Cp), 7.45 (m, 2, $C\underline{H}_2SBu$), 8.52 (m, 2, $FpC\underline{H}_2$), 8.77 (s, 9, Bu), (C_6D_6) τ (ppm) 5.70 (s, 5, Cp), 7.25 (m, 2, $C\underline{H}_2SBu$), 8.37 (m, 2, $FpCH_2$), 8.68 (s, 9, Bu).

Anal. found: C, 53.07; H, 6.06; S, 11.02. $C_{13}H_{18}FeO_2S$ calcd.: C, 53.01; H, 6.17; S, 10.90%.

Reaction of XIVa with trityl hexafluorophosphate

1-Fp-2-t-butylthioethane (0.160 g, 0.545 mmol) in 1 ml CH_2Cl_2 was treated with a solution of tritylPF_6 (0.205 g, 0.53 mmol) in 4 ml of CH_2Cl_2 at 0°C. A precipitate formed immediately and after 30 minutes 25 ml of ether was added. This material was identified as Fp(ethylene)PF_6 0.155 g, (84%) by comparison of the IR and NMR with those of an authentic sample.

Preparation of 1-t-butylthio-2-Fp-propane (XIVc) and 2-t-butylthio-1-Fp-propane (XIVb)

To a suspension of Fp(propene)BF_4 (0.459 g, 1.5 mmol) and K_2CO_3 (0.207 g, 1.5 mmol) in 5 ml CH_3CN at 0°C was added t-butyl mercaptan (0.165 ml, 1.5 mmol). The resulting reaction mixture was stirred for 6 hours at room temperature during which time it changed color from orange to red. The mixture was filtered and stripped. The residue was chromatographed on 25 g activity III neutral alumina. Elution with ether gave the product as an orange oil, 0.360 g, (78%); IR (film) 2004, 1946 cm^{-1}; NMR (CS_2) τ (ppm) 5.30, 5.35 (two s, ratio 2.6:1, Cp), 7.0—7.7 (m, $\underline{H}C(CH_3)SBu$, $FpC\underline{H}(CH_3)$, one diastereotopic $C\underline{H}_2SBu$), 8.00 (dd, *J* 10.0, 4.0 Hz, one diastereotopic $C\underline{H}_2SBu$), 8.55—8.8 (m, Bu, $FpC\underline{H}_2$, CH_3).

Anal. found: C, 54.50; H, 6.28; S, 10.37. $C_{14}H_{20}FeO_2S$ calcd.: C, 54.56; H, 6.54; S, 10.40%.

Preparation of 1-t-butylthio-2-phenyl-2-Fp-ethane (XIVd)

The styrene complex Ic (184 mg, 0.5 mmol) was dissolved in 3 ml of acetonitrile at 0°C. Anhydrous K_2CO_3 (70 mg, 0.5 mmol) was added and then t-butyl mercaptan (45 mg, 0.5 mmol). The solution was stirred for 2 h at room temperature. Anhydrous ether was then added; the mixture was filtered and the precipitate was washed with ether. Concentration of the filtrate left an orange oil, which was chromatographed on 15 g of neutral activity III alumina to give 154 mg (86%) of XIVd as an orange oil; IR (film) 2004, 1945 cm^{-1}; IR (neat) 2010, 1940 cm^{-1}; NMR (CS_2) τ (ppm) 2.95 (m, 5, Ph), 5.6 (s, 5, Cp), 6.38 (dd, 1, *J* 12.5, 4.0 Hz, SCH_2), 6.7 (t, 1, *J* 12, 12 Hz, SCH_2), 7.05 (dd, 1, *J* 12,4 Hz, FpCH), 8.8 (s, 9, t-Bu).

Anal. found: C, 60.49; H, 6.04; S, 8.92. $C_{18}H_{22}FeO_2S$ calcd.: C, 60.34; H, 6.19; S, 8.95%.

Addition of triphenylphosphine to Ia. Formation of XVIa

A solution of Fp(ethylene)BF_4 (0.584 g, 2.0 mmol) in 2 ml CH_3NO_2 was treated with triphenylphosphine (0.526 g, 2.0 mmol) in small portions at room temperature. After 5 minutes reaction, the product was isolated by dropwise addition of the reaction solution to excess Et_2O at 0°C. The yellow solid obtained was recrystallized from CH_2Cl_2/Et_2O to provide 1.1 g (100%) of product as a brilliant yellow crystalline material, m.p. 172—173°C (gas evol.); IR (KBr) 2012, 1923 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 2.11—2.25 (m, 15, phenyl), 5.02 (s, 5, Cp), 6.66 (dm, 2, $C\underline{H}_2P$, *J*(P—H) 22 Hz), 8.58 (dm, 2, CH_2Fp, *J*(P—H) 18 Hz).

Anal. found: C, 58.63; H, 4.31; Fe, 9.96; P, 5.48. $C_{27}H_{24}BF_4FeO_2P$ calcd.: C, 58.60; H, 4.36; Fe, 10.09; P, 5.57%.

Phosphonium salt XVIa (0.554 g, 1.0 mmol) was added to a suspension of $LiAlH_4$ (0.040 g, 1.0 mmol) in 5.0 ml anhydrous Et_2O and the resulting reaction mixture was refluxed for 2 hours. Upon cooling, filtration provided the starting complex, 0.524 g, (95%). The filtrate was clear.

Phosphonium salt (XVIa) (0.554 g, 1.0 mmol) was added to a suspension of $LiAlH_4$ (0.040 g, 1.0 mmol) in 5.0 ml anhydrous THF and the resulting reaction mixture was refluxed for 3 hours. A tan solid slowly formed over this time. After cooling, filtration provided a tan solid, 0.475 g, (90%), identified as XVII; IR (KBr) 2058, 2020 cm^{-1}; NMR (CD_3NO_2) τ (ppm), 2.31 (m, 15, phenyl), 4.56 (d, 5, Cp, *J*(P—H) 2 Hz).

Phosphonium salt XVIa (0.277 g, 0.50 mmol) was dissolved in 0.50 ml $CHCl_3$ saturated with HCl and the solution was refluxed for 2 hours with continuous introduction of HCl. Addition of the reaction solution to excess Et_2O provided the starting complex (0.272 g, 98.4%).

Phosphonium salt XVIa (0.415 g, 0.75 mmol), LiF (0.039 g, 1.5 mmol), and benzaldehyde (0.10 ml, 1.00 mmol) were dissolved in 5 ml CH_3CN and the resulting solution was refluxed for 2 hours. The solution was cooled, filtered and the filtrate evaporated to leave the starting complex, 0.395 g (95%).

Addition of triphenylphosphine to Ib. Formation of XVIb

To a solution of Fp(propene)BF_4 (0.062 g, 0.20 mmol) in 0.30 ml CD_3NO_2 contained in an NMR tube was added triphenylphosphine (0.052 g, 0.20 mmol) neat. Monitoring of the reaction by NMR revealed reaction to be complete with-

in 15 minutes with the exclusive formation of XVIb. Unreacted phosphine and propene salt Ib were also observed; NMR (CD_3NO_2) τ (ppm) 2.00 (m, 15, phenyl), 4.83 (s, 5, Cp), 6.30 (m, 1, C<u>H</u>P), 8.40 (dd, 3, CH_3, J 21,7 Hz), 7.9—9.0 (m, 2, $FpCH_2$ diastereotopic); IR (KBr) 2012, 1953 cm^{-1}.

Attempted preparation of this phosphonium salt on a preparative scale at 0° or —16° C resulted in the formation of addition product XVIb along with $FpP(Ph)_3^+$ (XVII) and unreacted propene salt. Attempted purification by recrystallization of the crude product from methylene chloride/ether led to reversion to Ib and to XVII.

Preparation of 2-Fp-3-triphenylphosphonium propene tetrafluoroborate (XVIII)

A solution of $Fp(allene)BF_4$ (0.457 g, 1.5 mmol) in 10 ml dry acetone was treated with triphenylphosphine (0.393 g, 1.5 mmol) at 0° C. After stirring for 30 minutes, the product was isolated by dropwise addition of the reaction solution to an excess of cold (0° C) ether. The yellow solid obtained was recrystallized from CH_2Cl_2/Et_2O to provide fine light yellow crystals, 0.849 g (100%), m.p. 95° (dec.); IR (KBr) 2010, 1962 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 2.21 (s, 15, phenyl), 4.5 (d(br), 2, CH_2=, J 4 Hz), 4.94 (s, 5, Cp), 5.54 (d, 2, C<u>H</u>$_2$P, J 13.5 Hz).

Anal. found: C, 59.40; H, 4.25; P, 5.44. $C_{28}H_{24}BF_4FeO_2P$ calcd.: C, 59.41; H, 4.27; P, 5.47%.

Preparation of diethyl-2-Fp(ethyl)phosphonate (XX)

A solution of $Fp(ethylene)BF_4$ (0.584 g, 2.0 mmol) in 3 ml of CH_3NO_2 was treated with triethyl phosphite (0.322 g, 2.0 mmol) at room temperature. The initial yellow color of the solution lightened slightly. After 1 hour the solution was filtered and solvent removed under high vacuum to provide the product XIX as an orange oil, 0.885 g (97%); IR (film) 2010, 1949 cm^{-1}; NMR (CD_3NO_2) τ (ppm) 4.88 (s, 5, Cp), 5.35 (five lines, J 7.0 Hz, 6, $OC\underline{H}_2CH_3$), 7.47 (m, 2, $C\underline{H}_2P$), 8.47 (t, 9, $OCH_2C\underline{H}_3$, J 7.0 Hz), 8.47 (m, 2, $FpC\underline{H}_2$). Without further purification the adduct (0.88 g, 1.93 mmol) was warmed in 2 ml of DMSO containing LiCl (0.126 g, 3.0 mmol) at 60° C for 1 hour. The reaction mixture was poured into 10 ml of CH_2Cl_2 and washed with water. After workup, the residual oil was chromatographed on 10 g activity III neutral alumina. Elution with CH_2Cl_2 gave a broad yellow-orange band yielding XX as a viscous dark orange liquid, 0.503 g (74%); IR (film) 2000, 1938 (C≡O), 1220—1205 (P=O), 1053, 1026, 962 (P—O) cm^{-1}; NMR (CS_2)τ (ppm) 5.23 (s, 5, Cp), 6.00 (five lines, 4, $OC\underline{H}_2CH_3$, J 7.0 Hz), 8.2 (m, 1, CH_2P), 8.48 (s, 2, CH_2Fp), 8.76 (t over m, 7, $OCH_2C\underline{H}_3$, J 7.0 Hz, CH_2P).

Anal. found: C, 45.52, 45.47; H, 5.77; 5.82; P, 8.90, 8.94. $C_{13}H_{19}FeO_5P$ calcd.: C, 45.64; H, 5.60; P, 9.05%.

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