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THE MECHANISM OF (1,3) SIGMATROPIC SHIFT IN η^5-$C_5H_5Fe(CO)(L)(\eta^1$-ALLYL) COMPLEXES

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Summary

$CpFe(CO)[P(OCH_2)_3CCH_3](\eta^1$-allyl) complexes undergo (1,3) sigmatropic shift of the Fe—C bond at rates considerably lower than those observed for the corresponding $CpFe(CO)_2(\eta^1$-allyl) complexes. The mechanism of this process is not intramolecular, as shown by crossover experiments. The results are in accord with a radical chain process, involving the $CpFe(CO)(L)$ radical as chain carrying species and S_H2' addition of this radical to $CpFe(CO)(L)(\eta^1$-allyl).

Introduction

Sigmatropic (1,3) rearrangements, especially those involving migrating groups other than carbon or hydrogen [1], are well known for a number of main group elements including magnesium [2], zinc [3], cadmium [4], mercury [5], boron [6], silicon [7], tin [8] and sulfur [9]. Ionic equilibria provide the mechanism for exchange for the more electropositive of these elements, but allylboron, -silicon, -sulfur and -mercury compounds appear to undergo rearrangement by concerted unimolecular and bimolecular processes. While *d*-orbital interactions may in principle promote the reactions of third or higher row main group elements through a *trihapto* intermediate, there is little evidence for this [10]. By contrast, stable *trihapto*allylmetal complexes, for which the related *monohapto*-allylmetal complex often represents an unstable, but thermally accessible state, are commonplace among transition metal complexes. The fluxional character of these has been extensively examined [11], but much less is known of the sigmatropic behavior of *monohapto*allyl transition metal complexes. Of these, a number of 4-coordinate η^1-allylpalladium complexes with bidentate chelating ligands undergo rapid (1,3) sigmatropic shift, possibly, through an $\eta^1 \rightleftharpoons \eta^3$ equilibrium [12]. However, such a pathway may not be as accessible to coordinatively saturated complexes. For example, $CpFe(CO)_2(\eta^1$-1-indenyl) shows no

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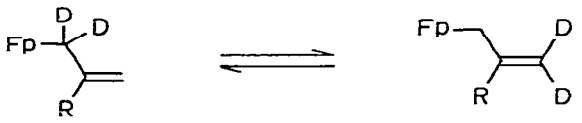
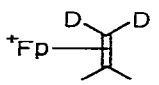
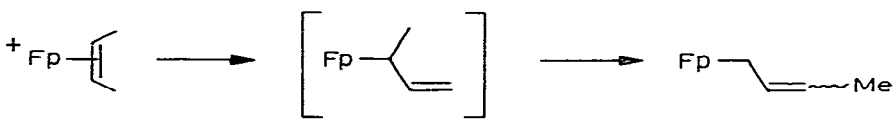
dynamic behavior on the NMR time scale up to temperatures of 70°C [13]. The closely related $CpFe(CO)_2(\eta^1$-allyl) complexes are likewise nonfluxional at normal temperatures. Yet evidence for kinetically facile (1,3) migrations in these latter complexes derives from a number of observations. Merour and Cadiot [14] have reported equilibration of Ia and IIa at room temperature, and we have observed that deprotonation of the labelled isobutylene complex III, under comparatively mild conditions, gave the fully equilibrated mixture of isobutenyl complexes Ib and IIb [15]. [Fp = $CpFe(CO)_2$].





a, R = H
b, R = Me

Furthermore, deprotonation of the *cis*-2-buteneiron complex IV, was found to give a mixture of the *cis*- and *trans*-2-butenyliron complexes VI rather than the anticipated α-methallyliron complex V [15].



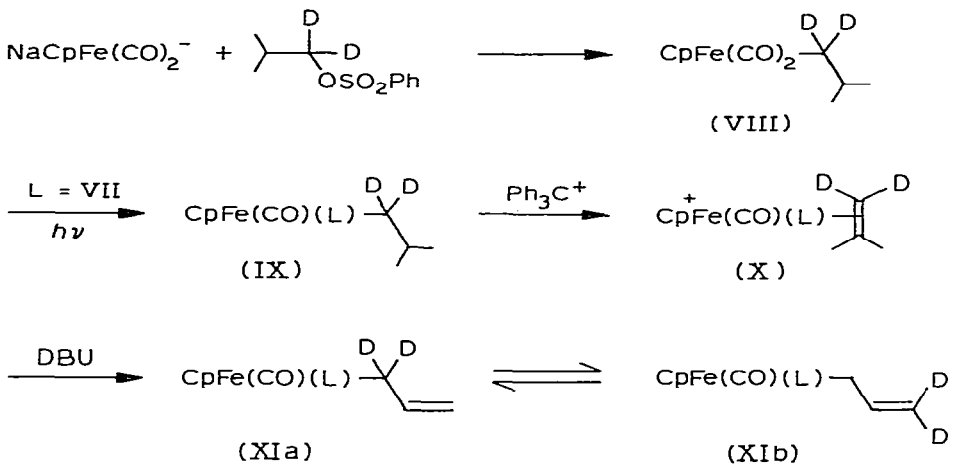
Results and discussion

In examining the mechanism of these reactions, we chose initially to study the closely related phosphite-substituted complexes [$CpFe(CO)(P(OR)_3)(\eta^1$-allyl)], since the metal—allyl carbon bond in these substances appears to be considerably stronger than in the parent complex [16], and we therefore anticipated a more favorable opportunity for examining the isomerization reaction kinetically. Moreover, the presence of a chiral metal center in the phosphite-substituted complexes would make it possible in principle to examine the stereochemistry of any nondissociative process taking place at this center.

Of these phosphite-derived allyliron complexes, those substituted by the bicyclic phosphite [$P(OCH_2)_3CCH_3$] VII [17] form unusually stable complexes [16]. The phosphite-substituted analog of Ib was accordingly prepared following the route employed earlier for the preparation of the parent substance

(Scheme 1) [15]. Metallation of 1,1-dideuterioisobutyl benzene sulfonate with NaFp gave VIII and this was converted to the phosphite-substituted complex IX by photochemically promoted ligand exchange [18]. As anticipated, no label scrambling occurs in this step. β-Hydride abstraction from IX, employing trityl tetrafluoroborate, gave the cationic complex X, again without detectable loss of label site specificity. This substance is a considerably weaker carbon acid than is the parent complex III and is consequently not deprotonated by triethylamine. However an equimolar amount of the stronger nitrogen base 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) effects rapid and complete deprotonation at room temperature. In contrast to the behavior of III, which yielded label-equilibrated products (I and II), X gave the specifically labelled complex XIa exclusively.

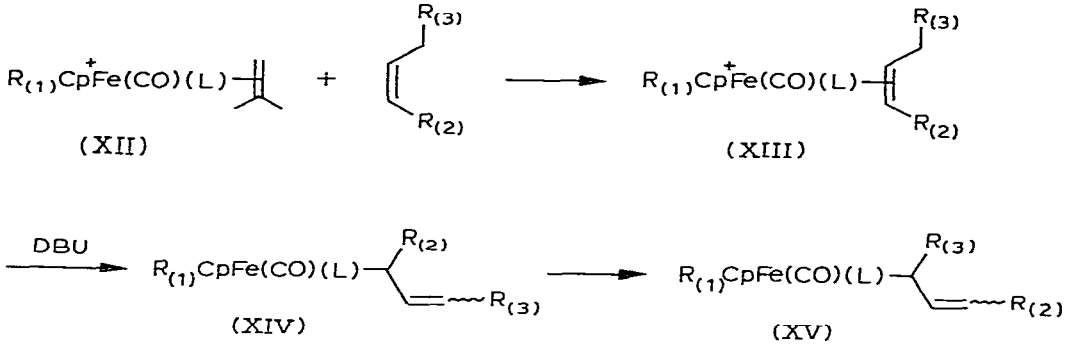
SCHEME 1



Although label scrambling through a formal (1,3) sigmatropic shift does occur in XIa, the reaction proceeds slowly even at elevated temperatures. After heating at 60°C in benzene solution for 68 hours, interconversion of XIa and IXb had proceeded no more than 10% to completion. Concurrent decomposition of starting material in these reactions and the long reaction times made it difficult to follow the reaction by NMR spectroscopy, and we therefore turned to an examination of the related nondegenerate reactions in these complexes. In the light of the above results, such systems, which would not require isotopic labelling, offered the additional advantage that conversion of a complex with a 2° carbon—metal to one with a 1° carbon—metal bond should be promoted and essentially irreversible.

The requisite system, an analog of complex V, is readily available through the *cis*-2-butene complex XIIIa which may in turn be prepared by an exchange reaction with the relatively labile isobutylene complex XIIa. Deprotonation of XIIIa was incomplete in the presence of one equivalent of DBU, but was rapid and complete at 0°C with three equivalents of this base. However, the product isolated from this reaction, after normal workup, was not the anticipated methallyl complex XIVa, but rather the rearranged product XVa, obtained as a 1 : 1 mixture of *cis* and *trans* isomers (Scheme 2).

SCHEME 2



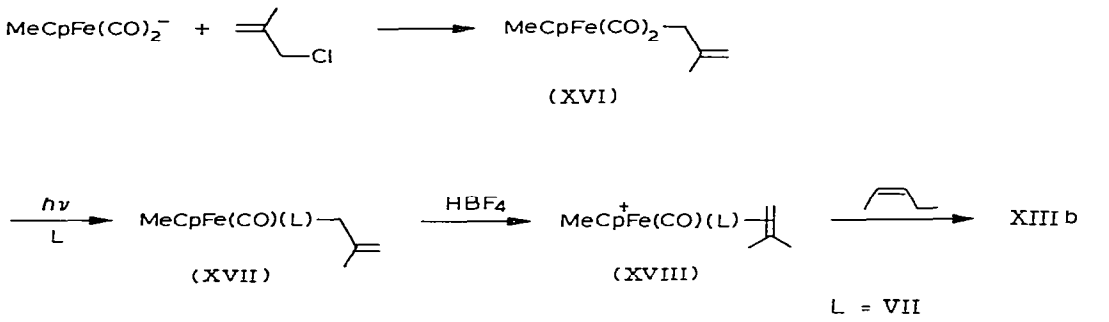
L = VII a, $R_{(1)}$ = H , $R_{(2)}$ = Me, $R_{(3)}$ = H ;
b, $R_{(1)}$ = Me, $R_{(2)}$ = Et , $R_{(3)}$ = H ;
c, $R_{(1)}$ = Me, $R_{(2)}$ = Me, $R_{(3)}$ = Me ;
d, $R_{(1)}$ = H , $R_{(2)}$ = Et , $R_{(3)}$ = H ;
e, $R_{(1)}$ = Me, $R_{(2)}$ = Me, $R_{(3)}$ = H ;

The formation of XIVa as an intermediate in the deprotonation of XIIIa can however be observed when the reaction is followed in an NMR experiment. At 37°C in CD_2Cl_2 solution, following the addition of excess DBU, the Cp proton doublet signal (J(PH) = 1 Hz) at δ 5.00 ppm of XIIIa, is rapidly replaced by two singlet resonances at δ 4.20 and 4.25 ppm assigned to Cp resonances in the two diastereomeric forms of XIVa. At the same time a low field multiplet at δ 6.30 ppm, associated with the 3° vinyl proton in intermediate XIVa, grows in. The slower conversion of XIVa to XVa is evidenced by progressive disappearance of the vinyl proton absorption at δ 6.30 ppm and its replacement by new vinyl proton resonances at δ 5.70 and 5.00 ppm. At the same time the Cp resonances of XIVa are replaced by new ones at δ 4.40 and 4.45 ppm. The half life for the conversion of XIVa to XVa may be estimated from this experiment to be approximately 15 minutes, but owing to the extensive overlapping of resonances it was not possible to reduce these observations to a more quantitative measurement of rates. Thus, while sigmatropic rearrangement is promoted in the complex with a 2° carbon—metal bond, kinetic determination of the order of the reaction, essential for distinguishing between an intra- and an intermolecular process, was not possible. We therefore sought to extract this information from a crossover experiment.

Since XIIIa would serve well as a precursor to one partner in these experiments, the second, closely related complex XIIIb was prepared as outlined in Scheme 3. Sodium amalgam reduction of $[MeCpFe(CO)_2]_2$ [19] and alkylation of the resulting complex anion with isobutenyl chloride gave XVI. Brief irradiation of XVI in the presence of phosphite VII and a trace of $[MeCpFe(CO)_2]_2$ gave XVII [16,20], and this was converted to the isobutylene complex XVIII by protonation with HBF_4. Finally, the transformation of XVIII to the cor-

responding 2-pentene complex XIIIb was readily achieved by heating this complex in the presence of excess *cis*-2-pentene.

SCHEME 3



Since base-promoted deprotonation of XIIIb can in principle proceed by loss of an allylic methyl or methylene proton to give XIVb and XIVc and thence by sigmatropic shift to XVb and XVc, respectively, we examined this reaction initially. Accordingly XIIIb was treated at 0°C in methylene chloride solution with excess DBU and the initial product was then allowed to equilibrate at room temperature for 24 hours. Examination of the NMR spectrum of the final product, after chromatographic purification, showed only the presence of complex XVb, as evidenced by the 3-proton triplet signal at δ 1.00 ppm, and the absence of any doublet signal near δ 1.50 ppm anticipated for XIVc, XVc. It is not clear from these results whether the outcome is a result of kinetically preferred deprotonation at the methyl group in XIIIb or to accumulation of the more stable complex possessing a 1° metal—carbon bond, by initial equilibration of XIVb and XIVc through the cation XIIIb.

Deprotonation of an equimolar mixture of cations XIIIa and XIIIb with excess DBU gave a mixture of allyl complexes. However, it was not possible to analyze the product mixture by examining its proton NMR spectrum, owing to extensive overlapping of resonances. Product identification was achieved instead through examination of the mass spectrum of the above reaction mixture and comparison of it with the mass spectra of the individual allyl complexes XVa and XVb. These data are summarized in Table 1.

The primary fragmentation pathways for XVa and XVb follow closely the pattern observed for a number of $CpM(CO)_nR$ complexes [21], especially the facile loss of CO from the parent ion, followed by loss of the allyl group. These fragmentation pathways are summarized in Scheme 4, and are confirmed for several of these transitions by the observation of metastable ions. The strength of the metal—phosphorus bond in these complexes is reflected in the prevalence of fragment ions which clearly retain the phosphite ligand.

The mass spectrum of the mixture of allyl complexes derived from the deprotonation of an equimolar mixture of the cations XIIIa and XIIIb, show, as anticipated, all of the primary fragment ions characteristic of products XVa and XVb. However, in addition to these, two new peaks at *m/z* 337 and 322 are present in the mass spectrum of the product mixture. The former is readily attributable to loss of CO from the parent ions of either of the crossover products XVd or XVe, while the peak at *m/z* 322 corresponds to the loss of methyl

TABLE 1

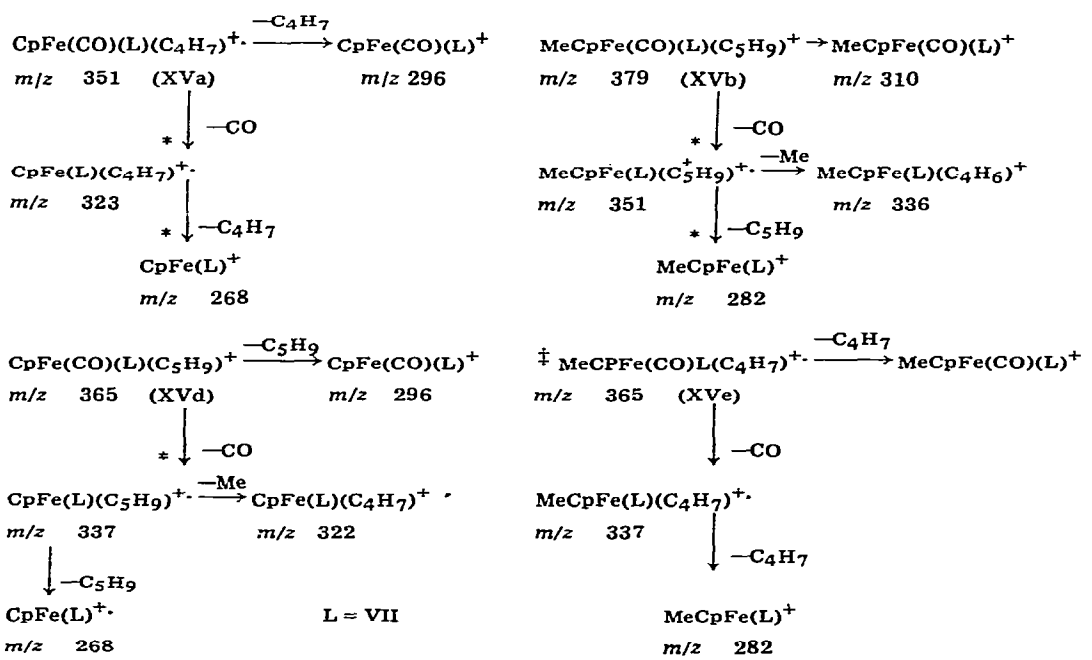
PRIMARY FRAGMENTATION PEAKS FOR RCpFe(CO)(L)(η^1-allyl) COMPLEXES [a]

	m/z (% rel. int.)			
Compound:	XVa	XVb	From Deprotonation of XIIIa and XIIIb	XVd
	323(100)	379(5)	379(1)	365(6)
	296(5)	351(100)	351(50)	337(100)
	268(70)	336(14)	337(100)	322(6)
		310(30)	336(20)	296(20)
		282(90)	323(80)	268(100)
		267(20)	322(10)	
			310(25)	
			296(20)	
			282(90)	
			268(90)	
			267(90)	

[a] Determined at 20 ev and at 65—70°C; L = VII.

from an *m/z* 337 fragment ion. This interpretation is confirmed by the mass spectrum of the allyl crossover complex XVd, prepared separately by the deprotonation of cation XIIId, which clearly show the peaks at *m/z* 337 and 322 in addition to those ions corresponding to fragmentation pathways defined for

SCHEME 4



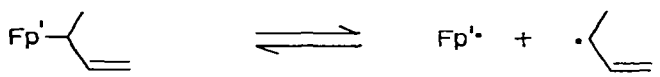
* Metastable peaks for these transitions were observed.

‡ Anticipated fragmentation pattern for this parent ion.

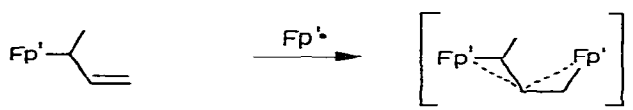
XVa and XVb. Moreover, the methyl group which is lost in the decomposition of both XVb and XVd must be assigned to fragmentation of a C_5H_9 ligand rather than to either the phosphite or MeCP ligands since the loss of methyl is not observed in XVa but is in XVd.

Finally, it may be shown that product scrambling does not occur as an artifact in the mass spectrometer due to ion—molecule reactions, since the mass spectrum of a separately obtained equimolar mixture of the allyl complexes XVa and XVb is simply a composite of the spectrum of each.

These results serve to exclude intramolecular mechanisms for (1,3) sigmatropic shifts in these phosphite complexes, whether of form $\eta^1 \rightleftharpoons \eta^{1'}$ or of $\eta^1 \rightleftharpoons \eta^3 \rightleftharpoons \eta^{1'}$, since neither provides a pathway for ligand exchange competitive, if not coincident, with isomerization. The experimental results are most compatible with the radical chain mechanism summarized below (eq. 1—3), in which the chain-carrying species is the relatively stable Fp′ = CpFe(CO)(L) radical. The intensity of the *m/z* 337 fragment ion derived from the cross-coupled products XVd and XVe, compared with that of the similarly derived ($P - CO$) ions from XVa and XVb, suggests that the S_H2' process depicted in eq. 2 competes effectively with radical recombination within the solvent cage.



(1)

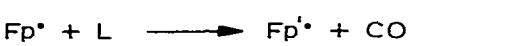


(2)

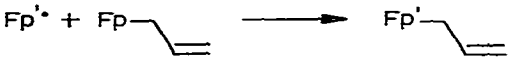
(3)

This mechanism is closely related to that recently proposed by Fabian and Labinger [22] for the photochemical initiated substitution of CO by phosphite in Fp(η^1-Cp) and Fp(η^1-allyl) complexes (eq. 4—6). The chain carrying species here is the Fp radical generated by photodissociation of traces of Fp_2 [23] added to the reaction mixture. Organometallic radical exchange takes place, as in eq. 2, by an S_H2' process, possibly involving a discrete intermediate as depicted above.

(4)



(5)



(6)

Radical chain processes had earlier been shown to be involved in carbonyl ligand substitution for a number of dinuclear metal carbonyl and metal carbonyl hydride complexes [24].

Further evidence in support of a radical chain process for 1,3-shifts in CpFe(CO)(L)(η^1-allyl) complexes is provided by the observation that the (1,3) sigmatropic shift in XIa, which takes place slowly (10% label equilibration at 60°C in 68 h), is greatly accelerated when solutions of XIa are irradiated in the presence of trace quantities of Fp_2 (34% label equilibration at 0°C after 15 min).

In conclusion, the evidence excludes intramolecular processes for the observed (1,3) sigmatropic shifts in CpFe(CO)(L)(η^1-allyl) type complexes, but is in accord with a radical chain process, in which the chain-carrying species, CpFe(CO)(L), can be generated either thermally or photochemically. Although the closely related $CpFe(CO)_2(\eta^1$-allyl) complexes were not examined in this work, it seems probable that these too undergo sigmatropic shift by a similar mechanism. Their much greater thermal lability compared with the phosphite-substituted complexes is in accord with the expectation of greater Fe—C bond strength for the latter substances [25], and may be inferred from the high stability of these complexes to thermal decomposition [16].

Experimental

All reactions and subsequent manipulations were carried out in a nitrogen atmosphere. Solvents were routinely dried by standard procedures, maintained under nitrogen over molecular sieves and degassed only by passing through a stream of nitrogen prior to use unless otherwise noted. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer model 457. ^{1}H NMR spectra were recorded on either a Varian A-60 spectrometer (NIH G-13183), a Perkin-Elmer R-32 spectrometer (NSF GU 3852) or a Bruker WH-90 spectrometer (NSF GU 3852, GP 37156). Mass spectra were determined on an AEI MS-12 spectrometer (NSF GP-3644). Melting points were determined in sealed capillaries or under nitrogen and are uncorrected. Elemental analyses were determined by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Preparation of $CpFe(CO)[P(OCH_2)_3CCH_3]CD_2CH(CH_3)_2$ (IX)

A solution of (1,1-dideuterioisobutyl)Fp, VIII, (2.0 g, 8.6 mmol) and VII (1.2 g, 8.6 mmol), in 40 ml of a 3 : 2 petroleum ether (20—40°C)-benzene solution, was irradiated with a 275 Watt Sylvania Sunlamp for 10.5 h, while the temperature of the solution was maintained between 10 and 25°C. Solvent was then removed in vacuo and the residue was taken up in methylene chloride and filtered through neutral alumina (Act IV, 3 × 3 cm). Removal of solvent left an oily solid, which on addition of petroleum ether gave 2 g (67%) of product as a yellow, air stable solid: IR (CH_2Cl_2) 1920 cm^{-1}; NMR (CS_2) δ 4.35 (d, 5, J(PH) = 1 Hz, Cp), 4.08 (d, 6, J(PH) = 6 Hz, OCH_2) 1.5—0.9 (m, 7, CH, CH_3), 0.85 ppm (s, 3, CH_3).

Preparation of $CpFe(CO)[P(OCH_2)_3CCH_3][\eta^2$-$CD_2$=$C(CH_3)_2]BF_4$ (X)

Trityl tetrafluoroborate (1.9 g, 5.7 mmol) dissolved in a small volume of methylene chloride was added to a solution of IX (2.0 g, 5.6 mmol) in 70 ml of

methylene chloride cooled to 0°C. The solution was stirred at 0°C for 5 min and then at room temperature for 1 h. Solvent was removed, the residue was dissolved in acetone and then filtered through $MgSO_4$. Addition of ether to the filtrate precipitated an orange-yellow solid. Reprecipitation of this material four times from methylene chloride by addition of ether gave 1.67 g of product (67%). Comparison of the NMR spectrum of this material with nondeuterated material [16] shows that the olefin is more than 98% deuterated at C(1); NMR (CD_3NO_2) δ 5.28 (d, 5, J(PH) = 1 Hz, Cp), 4.45 (d, 6, J(PH) = 6 Hz, OCH_2), 2.00 (s, 3, $CH_3C=$), 1.65 (d, 3, J(PH) = 3 Hz, $CH_3C=$), 0.85 ppm (s, 3, CH_3).

Deprotonation of X

The olefin salt X (0.329 g, 0.74 mmol) was dissolved in 30 ml of methylene chloride at 0°C. A solution of diazabicycloundecane (0.113 g, 0.74 mmol) in a small volume of methylene chloride was added to this and the solution was stirred at 0°C for 10 min and then at room temperature for 20 min. Solvent was removed, the residue was extracted with ether and the combined extracts were filtered through basic alumina (activity V). Removal of solvent left an oily solid which was recrystallized from ether-petroleum ether at −78°C, affording 0.20 g of XIa as a yellow solid (77%). An NMR spectrum of the product and comparison with that of unlabelled complex [16] showed the olefin to be greater than 98% deuterated at C(3).

Thermal isomerization of $CpFe(CO)[P(OCH_2)_3CCH_3][\eta^1\text{-}CD_2C(CH_3)=CH_2]$

A solution of XIa (0.259 g, 0.73 mmol) in 35 ml of dry, vacuum line-degassed benzene was stirred at 60°C for 68 h. The solution was then passed through a short column of basic alumina (activity V), eluting with ether. Removal of solvent left 0.225 g (87% recovery) of a yellow solid which was shown by NMR spectroscopy to be a mixture of starting material (XIa) and the 1,1-dideuterio-isobutenyl complex (XIb). Analysis of the NMR spectrum showed the label to be approximately 10% scrambled.

Photolysis of $CpFe(CO)[P(OCH_2)_3CCH_3][\eta^1\text{-}CD_2C(CH_3)=CH_2]$

A solution of XIa (0.260 mg, 0.74 mmol), in 20 ml of a 1 : 1 benzene-methylene chloride solution, was photolyzed using a 275 watt Sylvania Sunlamp for 1 h at 0°C. Solvent was removed in vacuo, the residue was taken up in methylene chloride and chromatographed on basic alumina (activity V), eluting with a 1 : 1 mixture of petroleum ether-ether. The product recovered was obtained as a yellow solid. Its NMR spectrum, determined in benzene-d_6, showed that deuterium scrambling between C(1) and C(3) of the isobutenyl ligand was 10% complete.

In a second experiment photolysis was carried out as above, except that 5 mg of $[CpFe(CO)_2]_2$ was added to the reaction and photolysis was allowed to proceed for only 15 min. Workup as above gave 57% of recovery product in which deuterium scrambling was 31% complete. The extent of deuterium scrambling in these experiments were determined from the ratio of integrated resonances at δ 4.80 (one proton of $CH_2=$) and at 4.45 ppm (Cp), in C_6D_6 solution.

Preparation of cis-2-butene complex (XIIIa)

The isobutylene complex XIIa (1.915 g, 4.34 mmol) and 3.0 g of *cis*-2-butene

(53 mmol) dissolved in 60 ml of 1,2-dichloroethane was heated at 65°C for 2.5 h, in a round bottom flask mounted with a dry ice condenser on top of a water-cooled condenser. The solution was then concentrated to a volume of 20 ml, cooled to room temperature and petroleum ether was added. The orange solid which precipitated was collected and recrystallized from methylene chloride-ether to give 1.52 g (80%) of XIIIa as an orange crystalline solid: IR (CH_2Cl_2) 2020 cm^{-1}; NMR (acetone-d_6) δ 5.35 (d, 5, J = 1 Hz, Cp), 4.58 (d+m, 7, J = 6 Hz, $(CH_2O)_3$,CH=), 4.30 (m, 1, CH=), 1.75 (two d, 6, J = 5 Hz, 7 Hz, CH_3CH=), 0.90 ppm (s, 3, CH_3).

Anal. Found: C, 41.17; H, 5.02. Calcd. for $C_{15}H_{22}BF_4FeO_4P$: C, 41.05; H, 5.02%.

Deprotonation of $CpFe(CO)[P(OCH_2)_3CCH_3][\eta^2$-$CH_3CH$=$CHCH_3]BF_4$ (XIIIa)

The olefin salt XIIIa (0.300 g, 0.68 mmol) was dissolved in 30 ml of methylene chloride at 0°C. DBU (0.106 g, 0.70 mmol) was added and the solution was stirred at 0°C for 30 min. An IR spectrum of the reaction solution showed that deprotonation was incomplete since carbonyl absorption for the cationic (2020 cm^{-1}) as well as neutral complexes (1922 cm^{-1}) were observed. An additional 2 equivalents of DBU was added, and after a further 20 min at 0°C, the IR spectrum showed complete deprotonation. Solvent was removed and the residue was dissolved in ether and chromatographed on basic alumina (act. V). Elution with ether gave, after removal of solvent from the single band, 150 mg (64%) of an orange oil, which crystallized on standing at 0°C to a yellow solid. This was identified as a 1 : 1 mixture of *cis*- and *trans*-XVa: IR (CH_2Cl_2): 1922 cm^{-1}; NMR (CS_2) δ 5.50 (m, 1, CH=), 4.90 (m, 1, CH=), 4.30 and 4.25 (2s, 5, Cp), 4.15 (2d, 6, J = 6 Hz, $(OCH_2)_3$)), 2.0—1.4 (d+m, 5, $FeCH_2$ + CH_3CH=), 0.75 ppm (s, 3, CH_3). Decoupling of the resonance at δ 2.00 ppm (d) caused the multiplet at δ 4.90 ppm to collapse to a pair of doublets (J = 11.2, 15.2 Hz). Similar irradiation of the multiplet at δ 4.90 ppm caused the doublet at δ 2.00 ppm to collapse to a singlet.

Deprotonation of XIIIa was carried out in an NMR experiment as follows. The salt XIIIa (74 mg, 0.17 mmol) was dissolved in methylene chloride-d_2, cooled to 0°C and DBU (25 mg, 0.17 mmol) was added in an NMR tube. The NMR spectrum obtained initially showed a broad multiplet near δ 6.50 ppm, assigned to the 3°-vinyl proton in XIVa. An additional 2 equivalents of DBU were added, and over several hours the resonance at δ 6.50 ppm diminished in intensity while new absorptions, characteristic of *cis*- and *trans*-XVa, increased in intensity. After 24 h at 0°C only resonance due to vinyl protons in these latter complexes were observed.

Preparation of $MeCpFe(CO)_2(\eta^1$-$CH_2C(CH_3)$=$CH_2)$ (XVI)

Methallyl chloride (2.7 g, 0.03 mol) was added to a solution of sodio methylcyclopentadienide (0.03 mol) in 100 ml of THF, prepared by sodium amalgam reduction of 6 g (0.015 mol) of $[MeCpFe(CO)_2]_2$ [19], at —78°C. After warming to room temperature over a 1 h period, solvent was removed in vacuo and the residue was extracted with ether. Solvent was removed and the residue was chromatographed on neutral alumina (act. III). Elution with 5% ether-petroleum ether gave 5 g (68%) of the product as an amber oil; NMR (CS_2) δ 4.60 (m, 7, Cp + CH_2=), 2.10 (s, 2, CH_2), 1.80 (s, 3, CH_3), 1.65 ppm (broad s, 3, CH_3Cp).

Preparation of MeCpFe(CO)[P(OCH$_3$)$_2$CCH$_3$][η^2-CH$_2$=C(CH$_3$)$_2$]BF$_4$ (XVIII)

A solution of MeCpFe(CO)$_2$(η^1-methallyl) (5.00 g, 20.2 mmol), bicyclic phosphite VII (3.0 g, 20.2 mmol) and [MeCpFe(CO)$_2$]$_2$ [19] (0.05 g, 0.12 mmol) in 60 ml of a 1 : 1 methylene chloride-petroleum ether solution was irradiated with a 275 watt Sylvania Sunlamp for 1 h. Solvent was removed in vacuo and the resulting oil was taken up in methylene chloride and filtered through celite. The solution was cooled to —78°C and petroleum ether was added to precipitate 7 g (94%) of XVII as a yellow solid. Tetrafluoroboric acid (48%, 7 ml, 38.6 mmol) was added to a suspension of XVII in ether cooled to —78°C, and the mixture was then allowed to warm to room temperature. The orange solid which formed was collected and washed with ether. Recrystallization from methylene chloride-ether afforded 7 g (76%) of product as an orange solid: NMR (acetone-d_6) δ 5.55 (m, 1, Cp), 5.25 (m, 1, Cp), 5.10 (m, 2, Cp), 4.50 (d, 6, J = 7 Hz, (OCH$_3$)$_2$), 3.75 (s, 1, CH$_2$=), 3.05 (d, 1, J(PH) = 11 Hz, CH$_2$=), 2.15 (s, 3, CH$_3$Cp), 2.05 (s, 3, CH$_3$C=), 1.65 (d, 3, J(PH) = 1 Hz, CH$_3$C=), 0.90 ppm (s, 3, CH$_3$).

Anal. Found: C, 42.55; H, 5.30. Calcd. for C$_{16}$H$_{24}$BF$_4$FeO$_4$P: C, 42.40; H, 5.30%.

Preparation of MeCpFe(CO)[P(OCH$_2$)$_3$CCH$_3$][cis-η^2-CH$_3$CH=CHCH$_2$CH$_3$]BF$_4$ (XIIIb)

The preparation of this salt by the exchange reaction of MeCpFe(CO)[P(OCH$_2$)$_3$CCH$_3$][CH$_2$=C(CH$_3$)$_2$]BF$_4$ (XVIII) (1.4 g, 3.08 mmol) with *cis*-2-pentane (2.2 g, 31.7 mmol) was carried out as in the preparation of CpFe(CO)[P(OCH$_2$)$_3$CCH$_3$0][*cis*-CH$_3$CH=CHCH$_3$]BF$_4$ and gave 1.2 g (83%) of product: IR (CH$_2$Cl$_2$) 2005 cm^{-1}; NMR (CD$_3$NO$_2$) δ 5.40—5.30 (m, 1, Cp), 5.10 (m, 1, Cp), 4.85 (m, 1, Cp), 4.50 (2 d+m, 7, J = 7 Hz, (OCH$_2$)$_3$ + Cp), 4.00 (m, 2, CH=CH), 2.4—2.0 (s+m, 5, CH$_2$ + CH$_3$Cp), 1.70 (dd, 3, J = 4.5, 7 Hz, CH$_3$), 1.15 (t, 3, CH$_3$), 0.90 ppm (s, 3, CH$_3$).

Anal. Found: C, 43.30; H, 5.63. Calcd. for C$_{17}$H$_{26}$BF$_4$FeO$_4$P: C, 43.70; H, 5.56%.

Deprotonation of XIIIb. Formation of XVb

The olefin complex (0.35 g, 0.75 mmol), dissolved in 30 ml of methylene chloride at 0°C, was treated with DBU (0.340 g, 2.24 mmol). The solution was warmed to room temperature and stirred for 24 h. Solvent was removed and the resulting oil was dissolved in a minimum volume of methylene chloride and chromatographed on basic alumina (act. III, 30 × 4 cm). Elution with ether gave 0.110 g (40%) of an oil, identified as XVb: NMR (CS$_2$ + C$_6$D$_6$) δ 5.50 (m, 2, CH=CH), 4.5—4.00 (m, 4, Cp) 4.15 (two d, 6, (OCH$_2$)$_3$), 1.80 (s, 3, CH$_3$Cp), 1.9—1.1 (m, 4, CH$_2$), 1.00 (t, 3, CH$_3$), 0.60 ppm (s, 3, CH$_3$).

Deprotonation of a mixture of XIIIa and XIIIb

Equimolar quantities of salts XIIIa and XIIIb (0.746 mmol) dissolved in 20 ml of 1,2-dichloroethane (degassed on the vacuum line) at 0°C, were treated with DBU (0.680 g, 4.47 mmol). The solution was allowed to warm to room temperature and was stirred for 24 h. Solvent was removed and the residue was taken up in methylene chloride and chromatographed on basic alumina (act.

III, 30 × 3 cm). Elution with ether-petroleum ether (1 : 1) gave 0.25 g of a mixture of neutral allyl complexes.

Preparation of $CpFe(CO)[P(OCH_2)_3][cis\text{-}\eta^2\text{-}CH_3CH{=}CHCH_2CH_3]BF_4$ (XIIId)

The preparation of this salt by the exchange reaction, involving 1.40 g (3.17 mmol) of $CpFe(CO)[P(OCH_2)_3CCH_3][CH_2{=}C(CH_3)]BF_4$ and 2.20 g (30.9 mmol) of *cis*-2-pentene, was carried out as for the preparation of $CpFe(CO)[P(OCH_2)_3CCH_3]$ (*cis*-$CH_3CH{=}CHCH_3)BF_4$ and gave 1.28 g (89%) of a 1 : 1 mixture of diastereoisomeric olefin complexes: IR (CH_2Cl_2) 2005 cm^{-1}; NMR (CD_3NO_2) δ 5.20 (broad s, 5, Cp), 4.50, 4.52 (2 d, 6, J = 7 Hz, OCH_2), 4.00 (broad m, 2, CH=CH), 2.4—2.0 (broad m, 2, CH_2) 1.75 (overlapping d, 3, J = 7.0 Hz, CH_3), 1.15, 1.17 (2t, 3, CH_3), 0.92 ppm (s, 3, CH_3Cp).

Preparation of $CpFe(CO)[P(OCH_2)_3CCH_3]$(cis- and trans-$\eta^1$-$CH_2CH{=}CHC_2H_5$) (XVd)

The olefin complex XIIId (1.0 g, 2.19 mmol), dissolved in 25 ml of methylene chloride at 0°C, was treated with DBU (1 g, 6.59 mmol). The solution was then allowed to warm to room temperature and was stirred for 15 h. Solvent was removed and the resulting oil was dissolved in a minimum volume of methylene chloride and chromatographed on basic alumina (act. III, 45 × 4 cm). Elution with ether gave 0.30 g (37%) of product as an amber oil: NMR (CS_2 + C_6D_6) 5.6—4.6 (broad m, 2, CH=CH), 4.35, 4.25 (2s, 5, Cp), 3.95 (2d, 6, OCH_2), 2.1—1.3 (broad m, 4, CH_2), 0.90 (t, 3, CH_3), 0.60 ppm (s, 3, CH_3).

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