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Mechanism of the Metathesis between Carbon Tetrachloride and (η^1-Allyl)iron Complexes. A Radical Chain Reaction of Overall Five-Thirds Order

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Chemical, kinetic, and stereochemical studies of the metatheses between CCl_4 and η-CpFe$(CO)_2CH_2CH{=}CR_2$ (R = H, Me) show that the reaction proceeds via a radical chain mechanism that involves the generation of the initiating radicals by a prequilibrium homolysis of the iron–allyl bond in the starting material. The ultimate product is formed by an S_H2' reaction between $^{\bullet}CCl_3$ and η-CpFe$(CO)_2CH_2CH{=}CR_2$. The reaction follows a rate law with an unusual $^5/_3$ total order: rate = $k_{obsd}[\eta\text{-CpFe(CO)}_2CH_2CH{=}CH_2][CCl_4]^{2/3}$.

Introduction

The metatheses between allyltin(IV)[1] or -cobalt(III)[2] compounds and certain organic halides is a mild chemo- and regiospecific method for the formation of carbon–carbon bonds at the γ-carbon of the allyl ligand (eq 1).

$$[M]{-}CH_2CR^1{=}CR^2R^3 + R^4X \rightarrow [M]{-}X + CH_2{=}CR^1CR^2R^3R^4 \quad (1)$$

$$[M] = SnR_3 \text{ or } LCo(dmg)_2$$

A number of observations indicate that these reactions occur, in many instances, via radical chain mechanisms involving the S_H2' displacement of the metal from the allyl ligand by an organic radical. For example, Johnson[2] observed that the reactions are accelerated photochemically and by the addition of radical initiators. Furthermore it was suggested that the homolysis of the weak cobalt–allyl bond in (allyl)Co(L)$(dmg)_2$ may provide, in part, the requisite radicals for the initiation of the chain. Although the chain-terminating steps of the reaction remain obscure the coupling of the alkyl radical R$^{\bullet}$ and $^{\bullet}$Co(L)$(dmg)_2$ may be important. Kinetic analysis of these reactions has not been reported.

We became interested in the S_H2' reactions of allylmetal complexes when during our investigations into the redox chemistry of (η^1-allyl)iron complexes we observed coupling products that appeared to involve this reaction.[3] At the time it had not been reported that (η^1-allyl)iron complexes entered into this reaction. A preliminary investigation of the reactivity of these allyl complexes quickly demonstrated that they are at least as reactive as the analogous tin and cobalt compounds. Accordingly, we embarked on a program to study the scope and the mechanism of the metathesis between Fp(η^1-allyl) (Fp = η-$C_5H_5Fe(CO)_2$) complexes and organic halides. Herein, we report the results of our investigation into the mechanism of the addition of carbon tetrachloride to (η^1-allyl)iron complexes. In another paper we will report on the scope and utility of the reaction.

Results

The mechanistic details of the metatheses between organic halides and allyliron complexes were gleened primarily from studies of the reaction between $FpCH_2CH{=}CH_2$ and CCl_4. The results from the reactions between $FpCH_2CH{=}CMe_2$ and CCl_4 were used to establish the regiochemistry of the metatheses, while the reactions involving α-haloesters were used to establish the reactivity patterns of the organic halides and the stereochemistry at the substrate carbon.

The metatheses between $FpCH_2CH{=}CH_2$ and CCl_4 (eq 2), which goes to completion in 1–2 days at 25 °C, was followed by monitoring the appearance of the 575-nm absorption of FpCl. The reaction affords a limited number of volatile products that were readily characterized by gas chromatography as 4,4,4-trichlorobutene (75–85% based on the initial amount of complex employed) accompanied by traces of allyl chloride, hexachloroethane, and lesser amounts of 1,5-hexadiene (biallyl) and propene. The only organometallic product is FpCl. At no time was Fp_2 observed by infrared spectroscopy during the course of the reaction.

$$FpCH_2CH{=}CH_2 + CCl_4 \rightarrow \underset{75\text{–}85\%}{CH_2{=}CHCH_2CCl_3} + \underset{trace}{CH_2{=}CHCH_2Cl} + \underset{trace}{CH_2{=}CHCH_3} + \underset{trace}{C_2Cl_6} + \underset{trace}{CH_2{=}CHCH_2CH_2CH{=}CH_2} + FpCl \quad (2)$$

Kinetic data were obtained under pseudo-first-order conditions on acetonitrile solutions that were initially 0.5 M in CCl_4 and 8.8×10^{-3} to 5.0×10^{-2} M in $FpCH_2CH{=}$

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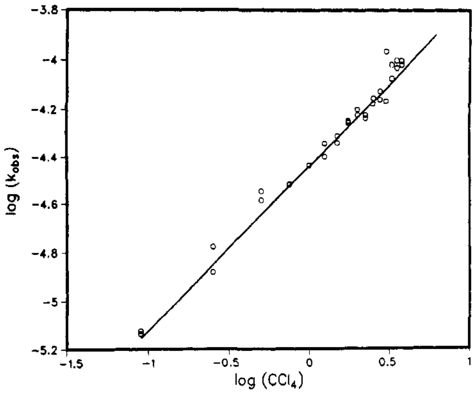

Figure 1. Plot of log k_{obsd} versus log $[CCl_4]$ for the reaction between CCl_4 and η-$CpFe(CO)_2CH_2CH{=}CH_2$.

CH_2. All reactions exhibit induction periods the duration of which are dependent on the initial concentration of $FpCH_2CH{=}CH_2$. These induction periods range from 24 h at low concentrations of the complex to 6 h when the concentration of the complex was 5.0×10^{-2} M. The reaction is uncontrollable when the complex is added to neat CCl_4 at 25 °C. After the induction period there ensues the more rapid propagation phase of the reaction. Data measured during the propagation phase were used in the kinetic analysis of the reaction. A plot of log $(A - A_t)$ versus time is linear over 2.5–3.0 half-lives of the reaction, thereby demonstrating that the reaction is first-order with respect to the complex. The values of the k_{obsd} are reproducible generally to within ±10%.

$$\text{rate} = k_{obsd}[FpCH_2CH{=}CH_2] \qquad (3)$$

where

$$k_{obsd} = k[CCl_4]^m \qquad (4)$$

An attempt was made to determine the order of the $[CCl_4]$ term in eq 3 by measuring the rate of reaction under conditions where the complex $FpCH_2CH{=}CH_2$ was present in tenfold excess. This experiment was thwarted by the formation of large amounts of Fp_2. The order of the reaction with respect to CCl_4 was determined under pseudo-first-order conditions by varying $[CCl_4]$ between 0.09 and 4.0 M. The concentration of CCl_4 was always at least 10 times greater than the concentration of the complex which ranged from 8.8×10^{-3} to 5.5×10^{-2} M. The slope of the plot of the 33 values of log k_{obsd} versus log $[CCl_4]$ was found to be 0.69 (Figure 1). The 95% confidence limits[4] are 0.66–0.73. This result indicates that the order of the reaction with respect to $[CCl_4]$ is far more likely to be $^2/_3$ rather than the expected[5] multiple of $^1/_2$. The intercept of −4.42 translates into a rate constant $k = 3.8 \times 10^{-5}\ M^{2/3}\ s^{-1}$. The rate of reaction is not significantly affected by the polarity of the solvents. In benzene, $k_{obsd} = 0.93 \times 10^{-5}\ s^{-1}[{}^{\bullet}CCl_3] = 0.5$ M), approximately one-third the rate observed in acetonitrile, $k_{obsd} = 2.6 \times 10^{-5}\ s^{-1}$, at 25 °C.

Reaction 2 was retarded by the addition of either radical scavengers or potential radical initiators such as benzoyl peroxide.[6] Thus, an acetonitrile solution of $FpCH_2CH{=}CH_2$ (5.0×10^{-2} M), CCl_4 (0.5 M), and galvanoxyl (1×10^{-3} M) was 70% unreacted after 96 h whereas a control experiment had gone to completion after only 30 h. A similar solution of complex and nitrosodurene (2.5×10^{-3} M) showed no evidence for the formation of FpCl after 96 h. A solution containing benzoyl peroxide (5×10^{-3} M) exhibited a short but rapid reaction followed by a 40-h induction period. There then ensued a propagation period which afforded $k_{obsd} = 3.5 \times 10^{-5}\ s^{-1}$—a value not very different from that obtained in the absence of the peroxide. The presence of Fp_2 in concentrations up to 8.8×10^{-4} M in acetonitrile shows no effect on k_{obsd}.

An acetonitrile solution of $FpCH_2CH{=}CH_2$ (0.1 M), CCl_4 (1.0 M), and nitrosodurene (0.005 M) exhibited an ESR spectrum, the intensity of which slowly increased with time. The spectrum consists of a triplet of triplets (A_N = 13.7 G, A_H = 10.3 G) centered at g = 1.9909. These values compare well with those reported for the allylnitroxyl radical (A_N = 13.57, A_H = 10.20, g = 2.0060).[7] No other resonances were observed. A benzene solution of $FpCH_2CH{=}CH_2$ and nitrosodurene exhibited the same set of resonances. A solution of CCl_4 and nitrosodurene in benzene does not exhibit an ESR signal.

The rates of the reaction between $FpCH_2CH{=}CH_2$ and ethyl haloacetates are dependent on the halogen. The iodoacetate required only 9 h for the reaction to go completion, the bromoacetate required 4 weeks, and the chloroacetate failed to react at 25 °C.

The regio- and stereochemistry of the reaction were investigated. 4,4,4-Trichloro-3,3-dimethyl-1-butene results from the metathesis between $FpCH_2CH{=}CMe_2$ and CCl_4 (eq 5). The nature of the product demonstrates that the

$$FpCH_2CH{=}CMe_2 + CCl_4 \rightarrow FpCl + CH_2{=}CHCMe_2CCl_3 \qquad (5)$$

addition of the trichloromethyl radical has occurred at the γ-carbon of the allyl ligand. The reaction between $FpCH_2CH{=}CH_2$ and methyl *d*-2-bromopropanoate (76% enantiomeric excess) affords a racemic metathesis product and racemic residual methyl *d,l*-2-bromopropanoate. The materials were collected after 4 days by gas chromatography and were analyzed by NMR spectroscopy using a chiral shift reagent.

Discussion

The results of our experiments clearly support the involvement of a radical chain reaction in the metathesis between the allyliron complexes and organic halides. Thus, the absence of a significant solvent effect on the rate of reaction, the stereorandom nature of the products, the inhibition of the reaction by radical scavengers, the trapping of the allyl radical by nitrosodurene, the observation of an induction period, and the detection of radical coupling products all lend strong support to the aforementioned mechanism. In addition the regiochemistry of the addition of CCl_4 to $FpCH_2CH{=}CMe_2$ suggests that the addition of the organic radical to the allyl ligand occurs via an S_H2' reaction.

The most notable feature of the reaction between $FpCH_2CH{=}CH_2$ and CCl_4 is the overall five-thirds order of the reaction—first-order with respect to complex and two-thirds order with respect to CCl_4. Apparently all other known radical chain reactions[5] exhibit total reaction orders of $n(^1/_2)$. We have considerable confidence in the validity of these results because of the number of measurements (vide supra) used in the analysis and the quality of the data. Scheme I accounts for all the experimental observations including the unusual reaction order.

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Scheme I

$$\mathrm{FpCH_2CH{=}CH_2} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Fp^{\bullet} + CH_2CH{=}CH_2^{\bullet}} \tag{6}$$

$$\mathrm{CH_2{=}CHCH_2^{\bullet} + CCl_4} \xrightarrow{k_2} \mathrm{CH_2{=}CHCH_2Cl + {}^{\bullet}CCl_3} \tag{7}$$

$$\mathrm{FpCH_2CH{=}CH_2 + {}^{\bullet}CCl_3} \xrightarrow{k_3} \mathrm{Fp^{\bullet} + CH_2{=}CHCH_2CCl_3} \tag{8}$$

$$\mathrm{Fp^{\bullet} + CCl_4} \xrightarrow{k_4} \mathrm{FpCl + {}^{\bullet}CCl_3} \tag{9}$$

$$\mathrm{{}^{\bullet}CCl_3 + {}^{\bullet}CCl_3} \xrightarrow{k_5} \mathrm{C_2Cl_6} \tag{10}$$

The derivation of the rate expression begins with the long chain approximation which equates the rates of the chain-propagating steps (eq 8 and 9) during the propagation of the reaction:[5]

$$k_3[\mathrm{FpCH_2CH{=}CH_2}][{}^{\bullet}\mathrm{CCl_3}] = k_4[\mathrm{Fp^{\bullet}}][\mathrm{CCl_4}] \tag{11}$$

Equation 11 is rearranged to yield an expression for [Fp$^{\bullet}$]:

$$[\mathrm{Fp^{\bullet}}] = \frac{k_3[\mathrm{FpCH_2CH{=}CH_2}][{}^{\bullet}\mathrm{CCl_3}]}{k_4[{}^{\bullet}\mathrm{CCl_3}]} \tag{12}$$

Invoking the steady-state approximation for [Fp$^{\bullet}$] and using the results of eq 12 gives an alternative expression for [Fp$^{\bullet}$]:

$$[\mathrm{Fp^{\bullet}}] = \frac{k_1[\mathrm{FpCH_2CH{=}CH_2}]}{k_{-1}[\mathrm{CH_2CH{=}CH_2}]} \tag{13}$$

During the propagation phase of the reaction the rate of formation of radicals equals the rate of termination. Half of the radicals come from reaction 7; therefore

$$k_2[\mathrm{CH_2{=}CHCH_2^{\bullet}}][\mathrm{CCl_4}] = k_5[{}^{\bullet}\mathrm{CCl_3}]^2 \tag{14}$$

$$[\mathrm{CH_2{=}CHCH_2^{\bullet}}] = \frac{k_5[{}^{\bullet}\mathrm{CCl_3}]^2}{k_2[\mathrm{CCl_4}]} \tag{15}$$

From eq 12 and 13 we have

$$\frac{k_3[\mathrm{FpCH_2CH{=}CH_2}][{}^{\bullet}\mathrm{CCl_3}]}{k_4[\mathrm{CCl_4}]} = \frac{k_1[\mathrm{FpCH_2CH{=}CH_2}]}{k_{-1}[\mathrm{CH_2CH{=}CH_2}]} \tag{16}$$

which is rearranged to give eq 17:

$$[\mathrm{CH_2{=}CHCH_2^{\bullet}}] = \frac{k_1k_4[\mathrm{CCl_4}]}{k_{-1}k_3[\mathrm{CCl_3}]} \tag{17}$$

Equations 15 and 17 are combined and solved for [$^{\bullet}$CCl$_3$] to give eq 18:

$$[{}^{\bullet}\mathrm{CCl_3}] = \left[\frac{k_1k_2k_4}{k_{-1}k_3k_5}\right]^{1/3}[\mathrm{CCl_4}]^{2/3} \tag{18}$$

The rate of the overall reaction during the propagation phase is the rate of reaction of (8) or (9).

$$\mathrm{rate} = k_3[\mathrm{FpCH_2CH{=}CH_2}][{}^{\bullet}\mathrm{CCl_3}] \tag{19}$$

Substituting for [$^{\bullet}$CCl$_3$] in eq 19 from eq 18 gives

$$\mathrm{rate} = \left[\frac{k_1k_2k_3{}^2k_4}{k_{-1}k_5}\right]^{1/3}[\mathrm{CCl_4}]^{2/3}[\mathrm{FpCH_2CH{=}CH_2}] \tag{20}$$

We are unable to locate in the literature other examples of radical chain reactions that exhibit orders that are multiples of $^1/_3$. The analysis of the kinetics of the photochemical chlorination of toluene by *t*-BuOCl gave an empirical rate equation that is two-thirds order in *t*-BuOCl:[8]

$$\mathrm{rate} = kI^{0.55}[\mathrm{RH}][t\text{-}\mathrm{BuOCl}]^{0.65} \tag{21}$$

The authors felt that the two-thirds order for the *t*-BuOCl term in eq 20 was probably 0.5 because of the error involved in their measurements. This interpretation may deserve a reexamination on the basis of our results. The N_2O_5-catalyzed decomposition of O_3 also gives rise to a rate expression that is two-thirds order with respect to the reactants.[9]

The five-thirds order for the reaction is a result of the preequilibrium reaction 6.[10] Since this sort of preequilibrium certainly is not unique to the iron system, there should exist a number of radical chain reactions that exhibit total reaction orders of $n(^1/_3)$.

Experimental

Materials. Both **FpCH$_2$CH=CH$_2$ and FpCH$_2$CH=CMe$_2$** were synthesized by the addition of the appropriate allyl halide to a THF solution of NaFp (prepared by the sodium amalgam reduction of Fp$_2$) at 0 °C.[11] After being stirred for several minutes, the resulting mixture was filtered and the filtrate concentrated by rotary evaporation. The residual oil was short path distilled to afford the allyl complex in better than 99% purity.

***d*-Methyl α-bromopropanoate** was prepared from *l*-lactic acid by the method of Cowdrey, Hughes, and Ingold.[12] The optical purity of this material and the products obtained from the metatheses between FpCH$_2$CH=CH$_2$ and *d*-methyl bromopropanoate was characterized by NMR spectroscopy using the chiral shift reagent Eu(tfc)$_3$.[13] **Ethyl iodoacetate** was obtained by treating ethyl chloroacetate with sodium iodide in acetone. **Nitrosodurene** was prepared by the method of Smith and Taylor from durene and isoamyl nitrite.[14]

The reaction products were isolated by initial percolation of the reaction mixture through alumina to remove nonvolatile organometallic and inorganic material. The eluate was then analyzed by gas chromatography, thereby allowing the isolation of the products and the determination of their yields. The products were characterized by comparison of their spectroscopic properties to literature values[1] or by comparison to the spectra of authentic materials.

Kinetic measurements were performed on acetonitrile solutions of FpCH$_2$CH=CH$_2$ or FpCH$_2$CH=CMe$_2$ under an argon atmosphere to which varying amounts of organic halide were added. The acetonitrile had been distilled from P_2O_5 and then degassed by the freeze–thaw method. The progress of each reaction was followed by monitoring the appearance of the 575-nm absorption of FpCl at 25 °C.

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Registry No. $FpCH_2CH{=}CH_2$, 38960-10-0; CCl_4, 56-23-5; $FpCH_2CH{=}CMe_2$, 38905-70-3; $CH_2{=}CHCH_2CCl_3$, 13279-84-0; $CH_2{=}CHCH_2Cl$, 107-05-1; C_2Cl_6, 67-72-1; $CH_2{=}CHCH_2CH_2CH{=}CH_2$, 592-42-7; $CH_2{=}CHCH_3$, 115-07-1; $CH_2{=}CHCMe_2CCl_3$, 61670-64-2; nitrosodurene, 38899-21-7; allyl nitroxyl radical, 116052-87-0; methyl *d*-2-bromopropanoate, 20047-41-0; ethyl iodoacetate, 623-48-3; ethyl bromoacetate, 105-36-2; ethyl chloroacetate, 105-39-5.

Chemistry of In-Plane Coordinated Double Bonds. Coordinated Alkyl and Aryl Migration to Adjacent Exocyclic Olefin in Alkyl(or aryl)halo(5-methylenecyclooctene)platinum(II)

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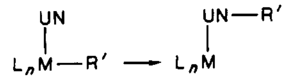
The complexes dichloro[(1,2,5,9-η^4)-5-methylenecyclooctene]platinum(II) (**4a**) and dibromo[(1,2,5,9-η^4)-5-methylenecyclooctene]platinum(II) (**4b**), each of which has an unusual "in-plane" coordinated olefin (C5C9), show marked reactivity enhancements compared to typical dihalo(η^4-diene)platinum(II) models. The second-order reaction of **4a** or **4b** with (aryl)$Sn(CH_3)_3$ results in aryl transfer to platinum with rate enhancement approaching 1000 compared to dichloro[(1,2,5,6-η^4)-cycloocta-1,5-diene]platinum(II) (**5**). The aryl or alkyl transfers to **4a** or **4b** are followed by rupture of the Pt(C5C9) π-olefin bond to form halide-bridged dimers, e.g. bis(μ-chloro)bis[(1,2-η^2)-5-methylenecyclooctene]diphenyldiplatinum(II) (**8**). The aryl groups transfer quantitatively from platinum to C9, with half-lives ranging from 7 to 110 min and with concomitant formation of a Pt–C5 σ bond (olefin "insertion" into Pt–aryl). Simultaneous coordination of olefinic C5C9 and aryl to Pt(II) is not observed directly; however, simultaneous coordination is observed when the transferred group is methyl. In the latter case the methyl group is observed to be trans to coordinated C5C9 and the subsequent methyl transfer to C9 has a methyl transfer half-life of 1.5×10^4 min (from **4a**) or 3×10^4 min (from **4b**). Also reported is the facile reaction of **4a** with sodium methoxide which results in formal insertion of C5C9 into Pt–OCH_3 (Pt–C5–C9–OCH_3). In the course of this work the crystal structures of derivatives of two final insertion products were determined. Crystal data for (benzylamine)chloro[(1,4,5-η^3)-1-(phenylmethyl)-4-cycloocten-1-yl]platinum(II) (**12**): $C_{22}H_{28}ClNPt$, space group $P\bar{1}$ with a = 10.613 (4) Å, b = 13.380 (5) Å, c = 7.969 (1) Å, α = 107.21 (2)°, β = 96.70 (2)°, γ = 108.56 (6)°, V = 996 (1) Å^3, Z = 2. Crystal data for chloro[(1,4,5-η^3)-1-(methoxymethyl)-4-cycloocten-1-yl](pyridine)platinum(II) (**16**): $C_{15}H_{22}ClNOPt$, space group $P2_1/n$ with a = 7.932 (3) Å, b = 17.619 (2) Å, c = 11.145 (2) Å, β = 101.16 (2)°, V = 1528 (1) Å^3, Z = 4.

Introduction

The migration of a coordinated ligand to an adjacent unsaturated (UN) cis ligand (e.g. eq 1) is one of the fundamental reactions in transition-metal organometallic chemistry.[3] For the specific case where UN = olefin, this type of insertion reaction has received extensive theoretical[4] and experimental[5] attention in the recent literature.



$$\overset{\text{UN}}{\overset{|}{\text{L}_n\text{M}}}\text{—R}' \longrightarrow \overset{\text{UN—R}'}{\overset{|}{\text{L}_n\text{M}}} \qquad (1)$$

In the special cases where UN = olefin, R′ = alkyl or aryl, and M = d^8 square planar (e.g. Pt(II)), it is expected that the ground-state conformation of the coordinated olefin would be perpendicular to the square plane containing the potential migration group (see **1**). There is universal agreement that ligand migrations to coordinated olefins would be facilitated by the "in-plane" olefin conformation in **2**, which prepares the system for the planar

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