Journal of Organometallic Chemistry, 144 (1978) 321—334
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MECHANISM OF THE THERMAL DECOMPOSITION OF $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1\text{-}$ACENAPHTHENYL)

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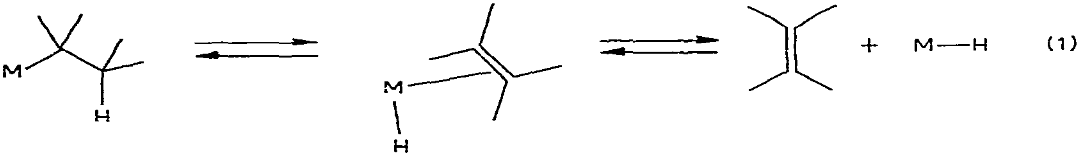
(Received August 10th, 1977)

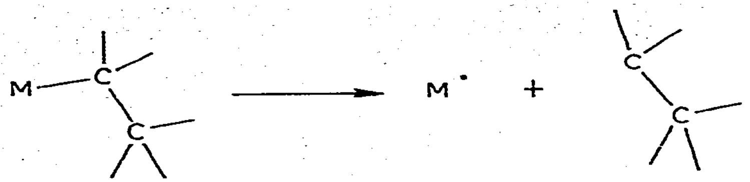
Summary

The complexes $(\eta^5\text{-}C_5H_5)Fe(CO)_2(\eta^1$-acenaphthenyl) (I), $(\eta^5\text{-}C_5H_5)Fe(CO)_2$ $(\eta^1$-*trans*-β-deuterioacenaphthenyl) (II), and $(\eta^5\text{-}C_5D_5)Fe(CO)_2(\eta^1$-acenaphthenyl) (XIII) have been prepared and their thermal decomposition studied in vacuo and in refluxing toluene. All three complexes decompose to produce mixtures of acenaphthene (VII), acenaphthylene (VIII), and $[C_5H_5Fe(CO)_2]_2$ (VI). Biacenaphthenyl (IX) is also obtained from the thermolysis of I in toluene. The formation of alkene VIII, and, to a lesser extent, alkane VII is suppressed by external CO. Thermolysis of I in toluene-d_8 and of II in vacuo and in toluene produces deuterium-enriched VII. The acenaphthene generated from the decomposition of XIII also contains deuterium. The above observations are accomodated by a mechanistic scheme involving competing β-elimination, iron—carbon bond homolysis to produce the acenaphthenyl radical, and Cp—H abstraction by an undetermined pathway.

The intermediacy of alkyl-transition metal compounds in numerous catalytic processes has encouraged mechanistic investigations of the reactions, including thermal decompositions, of isolable complexes possessing metal—carbon σ bonds [1—3]. The most common decomposition pathway appears to be β-hydride elimination which produces alkene and metal hydride as primary products (eq. 1) [4—6]. In some cases, the initially formed metal hydride may react further with remaining alkyl metal to produce alkane [5,7—9].



Metal—carbon bond homolysis (eq. 2) has been shown to occur in a few systems [10—14]. The resultant alkyl radicals may then undergo subsequent



(2)

reactions including dimerization, hydrogen abstraction and disproportionation. Other demonstrated reaction pathways include α-elimination [15—18] and hydrogen abstraction from a cyclopentadienyl ring [19—22].

For the most part investigations of the various factors determining which of several available decomposition pathways is favored are lacking. A study of the decompositions of a series of alkylmetal complexes where systematic variations are made in the alkyl group and associated ligands, therefore, would be highly informative. The (η^5-C_5H_5)Fe(CO)LR (L = phosphine, CO) complexes appear to be ideally suited for this purpose. These compounds are readily prepared by well-established routes [23—27] and they are generally quite stable including those containing secondary and tertiary alkyl groups. While chemically-induced cleavage reactions in this system have been studied intensively [28], until recently, the corresponding thermally-induced reactions had been largely ignored.

In an early report Wojcicki and Su [29] found that refluxing (C_5H_5)Fe(CO)(PPh_3)(C_2H_5) in toluene produced ethylene and (C_5H_5)Fe(CO)(PPh_3)H as the only identified products (eq. 3).

$$(C_5H_5)Fe(CO)(PPh_3)(C_2H_5) \xrightarrow{\text{toluene}} (C_5H_5)Fe(CO)(PPh_3)H + C_2H_4 \tag{3}$$

Recently, Reger and Culbertson [6] studied in some detail the thermal decomposition of several $C_5H_5Fe(CO)(PPh_3)R$ complexes (R = ethyl, n-butyl, sec-butyl, and isobutyl). Alkenes were the exclusive organic products of these reactions. Deuterium labeling and kinetic studies led to formulation of a mechanism involving reversible phosphine dissociation followed exclusively by β-elimination as outlined in eq. 4.

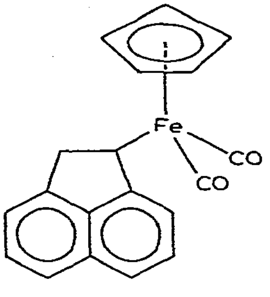
$$\begin{array}{lcl} (C_5H_5)(CO)Fe(PPh_3)(CH_2CH_3) & \rightleftharpoons & (C_5H_5)Fe(CO)(CH_2CH_3) + PPh_3 \\ & & \quad\quad\quad \upharpoonleft\!\downharpoonright \\ C_2H_4 + (C_5H_5)Fe(CO)(PPh_3)H & \xleftarrow{PPh_3} & (C_5H_5)Fe(CO)(CH_2CH_2)H \end{array} \tag{4}$$

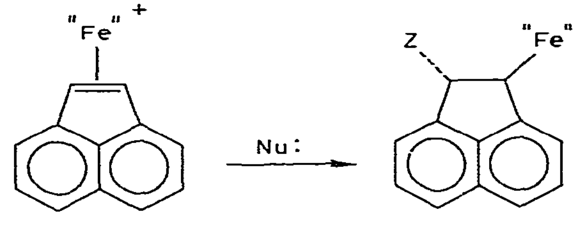
Less attention has been given to the related $C_5H_5Fe(CO)_2R$ complexes. Pittman and Felis [13] investigated the thermolysis of $C_5H_5Fe(CO)_2(CH_2Ph)$ and its polymer-bound analogue $C_5H_5Fe(CO)_2CH_2C_6H_4$-PS (PS = polystyrene). In both cases β-elimination is precluded and the observed products were derived largely from Fe—C homolysis and alkyl migration to the Cp ring (eq. 5). The yield of benzyl-containing material was quite low (ca. 30%).

$$\begin{array}{l} C_5H_5Fe(CO)_2(CH_2Ph) \xrightarrow{\Delta} PhCH_2CH_2Ph + \text{“tar”} + \\ \qquad\qquad [C_5H_5Fe(CO)_2]_2 + [(PhCH_2C_5H_4)Fe(CO)_2C_5H_5Fe(CO)_2] \end{array} \tag{5}$$

We have chosen to investigate the thermal chemistry of (C_5H_5)Fe(CO)$_2$-

(acenaphthenyl) (I), a system in which both β-elimination and metal—carbon bond homolysis should be facile. The parent compound I and various β-substituted derivatives e.g. II—IV. are readily prepared from the η^2-acenaphthylene complex V upon treatment with nucleophiles [27,30] (eq. 6). The stereospecific formation of *trans* products from this reaction provides a convenient route to


(I)



(V)

"Fe" ≡ $C_5H_5Fe(CO)_2$

(II) Z = D

(III) Z = $(CH_3)_3CS$

(IV) Z = $HCO(CH_3)_2C$

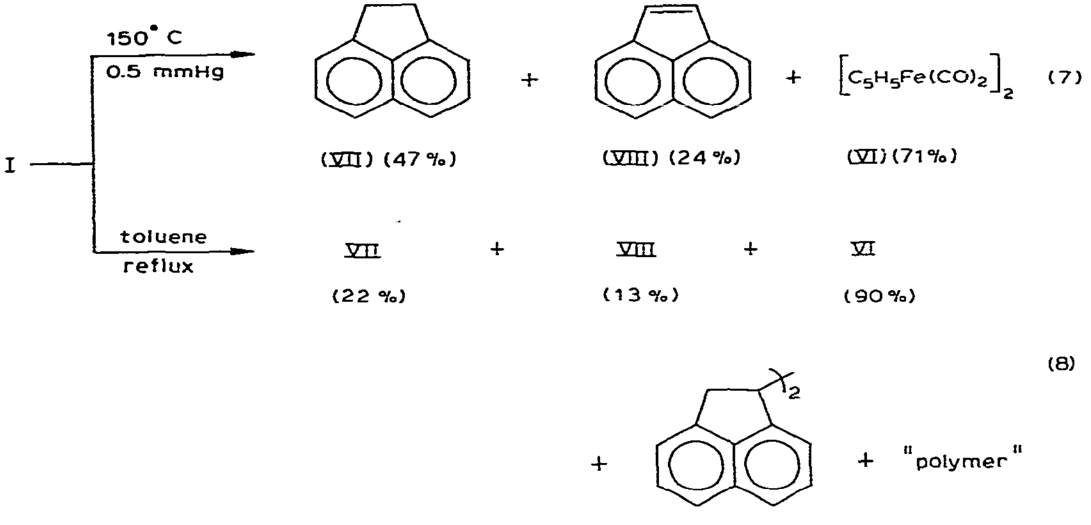
(6)

alkylirons of potential value in mechanistic studies of metal—carbon cleavage reactions. We also anticipated that organic products derived from the decomposition of I would be readily isolable and characterizable solids.

Results

The parent complex I was prepared in 77% yield from the reaction of V with $NaBH_3CN$ in acetonitrile solution. Crystalline I (m.p. 71—73°C) exhibited appropriate IR, NMR, and mass spectra and gave satisfactory analytical data.

The thermolyses of I and its derivatives to be discussed subsequently were carried out under two sets of conditions: (1) at 150°C in vacuo and (2) in refluxing toluene solution (110°C). The organic products were separated from $[(C_5H_5)Fe(CO)_2]_2$ (VI), the only identified organometallic product, by column chromatography. In both the vacuum and solution thermolyses formation of the alkane acenaphthene (VII) predominated over the alkene acenaphthylene (VIII) as shown in eqs. 7 and 8. From a large scale thermolysis of I in toluene biacenaph-



(VII) (47%) (VIII) (24%) (VI) (71%) (7)

(22%) (13%) (90%)

(8)

(IX) (11%)

thenyl IX was also isolated as well as some unidentified, possible polymeric, aromatic material.

The predominant formation of acenaphthene was rather unexpected. We therefore considered the possibility that acenaphthylene was being destroyed under the reaction conditions. To test this hypothesis an equimolar mixture of I and acenaphthylene was thermolyzed in vacuo. The mixture thus produced contained 70% acenaphthylene and 30% acenaphthene. If all of the additional VIII were recovered unchanged, a 73/27 ratio would be expected; the observed alkane/alkene ratio hence, does not result from partial destruction of VIII in a secondary reaction.

Since β-elimination to produce alkene from $C_5H_5Fe(CO)L(alkyl)$ should be preceded by ligand dissociation [6], the presence of an external ligand should inhibit alkene formation. We therefore investigated the effect of carrying out the decomposition of I under an atmosphere of carbon monoxide. When I was heated at 150°C under two atmospheres of CO, acenaphthene and acenaphthylene were again obtained but in a significantly increased ratio (4.5/1) and lower combined yield compared to the vacuum thermolysis results (eq. 9). External CO thus inhibits both acenaphthylene, and to a lesser extent, acenaphthene formation.

$$\begin{array}{llll} \mathrm{I} \xrightarrow[150^\circ]{\mathrm{CO}} & \mathrm{VII} & + & \mathrm{VIII} \\ & (22\%) & & (5\%) \end{array} \qquad (9)$$

Labeling experiments were devised in order to further elucidate the mechanism of these reactions and to determine the source of hydrogen atoms in the formation of acenaphthene.

The *trans*-β-deuterio compound II was prepared in 75% yield by treatment of the η^2-acenaphthylene complex V with $NaBD_3CN$. The assigned stereochemistry was based upon the magnitude of the coupling constant ($J < 2$ Hz) of the vicinal benzylic hydrogens [30], NMR integration of the benzylic versus aromatic protons of II indicated the incorporation of 0.90 ± 0.05 D/molecule.

When II was thermolyzed at 150°C/0.5 mmHg the acenaphthene/acenaphthylene ratio was again approximately 2/1. To determine the *d*-content of the products, the mixture was first separated by preparative GLC on diethylene glycol succinate/Chromosorb W. Careful NMR integration of the separated compounds showed that the acenaphthene contained 1.2 ± 0.10 D/molecule and that the acenaphthylene incorporated 0.6 ± 0.1 D/molecule (eq. 10).

$$\begin{array}{lllll} \mathrm{II} & \xrightarrow[0.5\,\mathrm{mmHg}]{150^\circ\mathrm{C}} & \mathrm{VII} & + & \mathrm{VIII} \\ 0.9\,\mathrm{D} & & 1.2\,\mathrm{D} & & 0.6\,\mathrm{D} \\ & & (41\%) & & (21\%) \end{array} \qquad (10)$$

It was apparent from this experiment that abstraction of hydrogen from the benzylic position had occurred in the production of acenaphthene. It was also clear that acenaphthylene was not produced solely by a *cis*-β-elimination pathway since if this were the case, it would contain 0.9 D/molecule.

The complex II was also decomposed in refluxing toluene. The deuterium content of the products from this reaction was found to be similar to that from the vacuum thermolysis of II as shown in eq. 11.

$$\mathrm{II} \xrightarrow[\text{reflux}]{\text{toluene}} \underset{\substack{1.1\ \mathrm{D} \\ (60\%)}}{\mathrm{VII}} + \underset{\substack{0.5\ \mathrm{D} \\ (40\%)}}{\mathrm{VIII}} \tag{11}$$

Once again the acenaphthene was somewhat deuterium-enriched relative to the starting complex while the acenaphthylene was deuterium-depleted. It is apparent, therefore, that β-hydrogen transfer plays a role in both the vacuum and solution thermolyses. It is also noteworthy that the same acenaphthene/acenaphthylene ratio (approximately 3/2) was observed in thermolyses of both the labeled and unlabeled complexes.

If iron—carbon bond homolysis were an important process in the decomposition of I, one might expect appreciable hydrogen atom abstraction by the acenaphthenyl radical from the solvent toluene. We assessed this possibility by thermolyzing I in toluene-d_8 (eq. 12). The acenaphthene/acenaphthylene ratio of 3/2 was essentially the same as in the corresponding reaction in undeuterated toluene, indicating a negligible isotope effect on the product distribution. While the acenaphthylene isolated was found to be devoid of deuterium, the acenaphthene contained 0.4 D/molecule.

$$\mathrm{I} \xrightarrow[\text{reflux}]{\text{toluene-}d_8} \underset{\substack{0.4\ \mathrm{D} \\ (17\%)}}{\mathrm{VII}} + \underset{\substack{0.0\ \mathrm{D} \\ (11\%)}}{\mathrm{VIII}} \tag{12}$$

One other reasonable hydrogen atom source was considered, the cyclopentadienyl ring. In order to detect Cp—H abstraction we prepared and thermolyzed the perdeuteriocyclopentadienyl complex XIII. The preparation of XIII was accomplished starting with perdeuterated cyclopentadiene according to equations 13—17. NMR integration of an equimolar mixture of the dimeric complex

$$\mathrm{C_5H_6} \xrightarrow[\mathrm{D_2O,DMSO}]{\mathrm{Na_2O_2}} \mathrm{C_5D_6} \tag{13}$$

$$\mathrm{C_5D_6} \xrightarrow{\mathrm{Fe(CO)_5}} \underset{(\mathrm{X})}{[(\mathrm{C_5D_5})\mathrm{Fe(CO)_2}]_2} \tag{14}$$

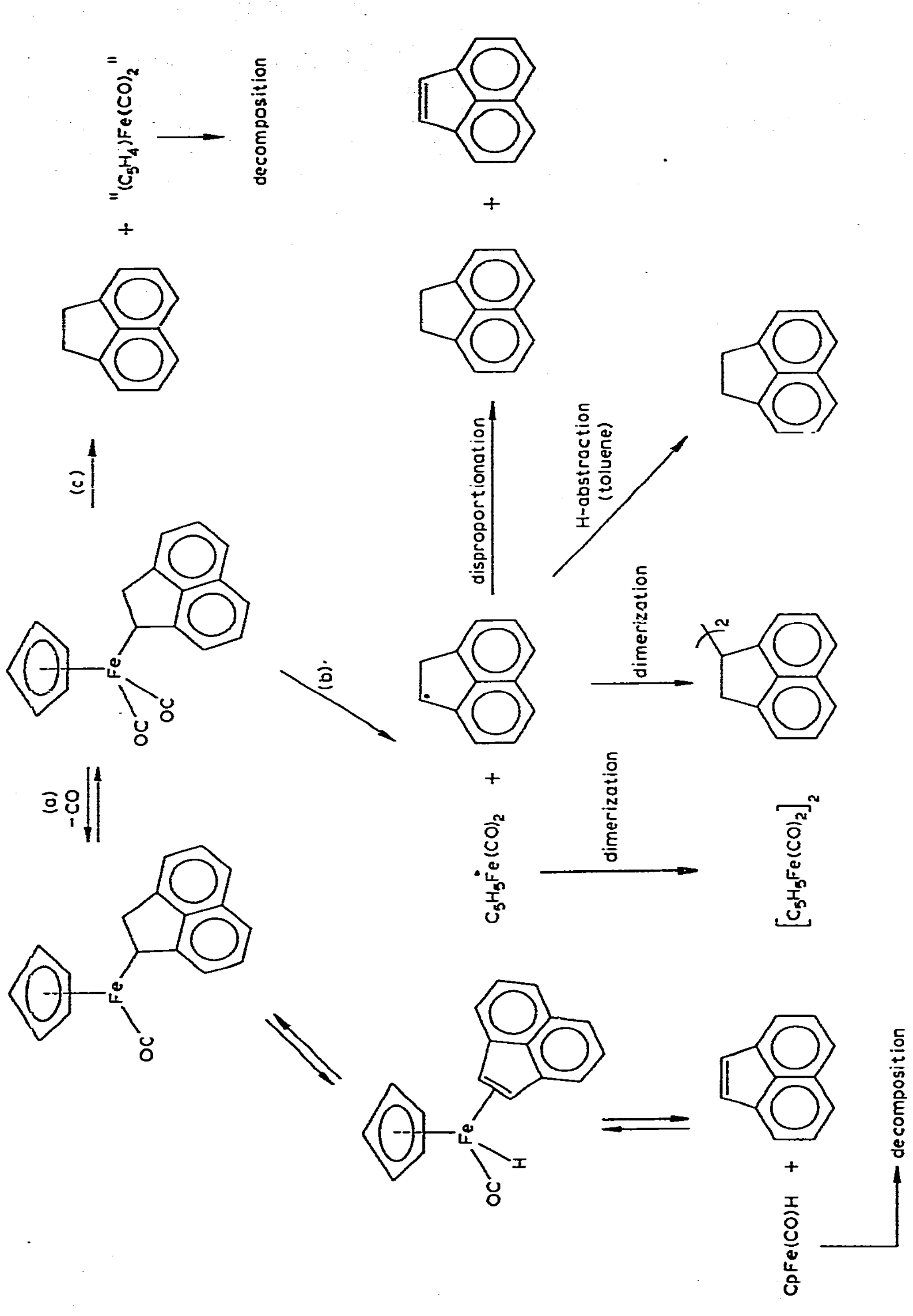
$$\mathrm{X} \xrightarrow[\substack{(2)\ \mathrm{ClCH_2C(CH_3){=}CH_2} \\ (3)\ \mathrm{HBF_4}}]{(1)\ \mathrm{Na/Hg}} \underset{(\mathrm{XI})}{(\mathrm{C_5D_5})\mathrm{Fe(CO)_2}[(\mathrm{CH_2{=}C(CH_3)_2}] + \mathrm{BF_4^-}} \tag{15}$$

$$\mathrm{XI} \xrightarrow{\mathrm{VIII}} \underset{(\mathrm{XII})}{(\mathrm{C_5D_5})\mathrm{Fe(CO)_2(acen)^+\ BF_4^-}} \tag{16}$$

$$\mathrm{XII} \xrightarrow[\mathrm{CH_3CN}]{\mathrm{NaBH_3CN}} \underset{(\mathrm{XIII})}{(\mathrm{C_5D_5})\mathrm{Fe(CO)_2}(\eta^1\text{-acenaphthenyl})} \tag{17}$$

X and naphthalene revealed that X contained approximately 4.0 D/Cp ring.

SCHEME 1.


Fe
OC
(a)
−CO
OC
OC
(c)
+
"(C5H4)Fe(CO)2"
decomposition
(b)
C5H5Fe(CO)2
+
disproportionation
+
H-abstraction
(toluene)
dimerization
dimerization
[C5H5Fe(CO)2]2
2
H
CpFe(CO)H
+
decomposition

Since reactions 15—17 presumably do not involve any exchange of the cyclopentadienyl hydrogens, the corresponding acenaphthenyl complex XIII was assumed to have the same deuterium content. When the thermolysis of XIII was carried out in vacuo, the acenaphthylene was shown by NMR analysis to be free of deuterium (0 ± 0.5 D) while the acenaphthene was found to contain 0.5 D/molecule (eq. 18). This result clearly demonstrates the occurrence of hydrogen abstraction from the cyclopentadienyl ring as one pathway for the formation of acenaphthene. The thermal decomposition of XIII was not studied in solution.

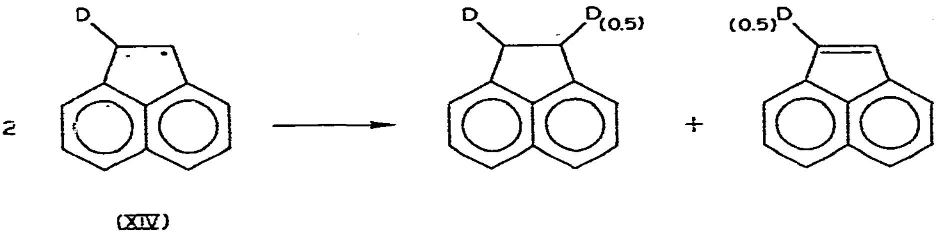
$$\text{XIII} \xrightarrow[\text{vacuum}]{150^\circ\text{C}} \underset{0.5\,\text{D}}{\text{VII}} + \underset{0.0\,\text{D}}{\text{VIII}} \qquad (18)$$

Discussion

It is appropriate at this point to summarize the key experimental results which any mechanistic scheme must rationalize: (1) acenaphthene (major), acenaphthylene (minor), and biacenaphthenyl (minor) are products; (2) carbon monoxide inhibits acenaphthylene formation; (3) the hydrogen atom required to produce acenaphthene may arise from three sources: (a) the benzylic position β to the iron, (b) the solvent toluene, and (c) the cyclopentadienyl ring. A mechanistic picture consistent with the above observations is presented in Scheme 1.

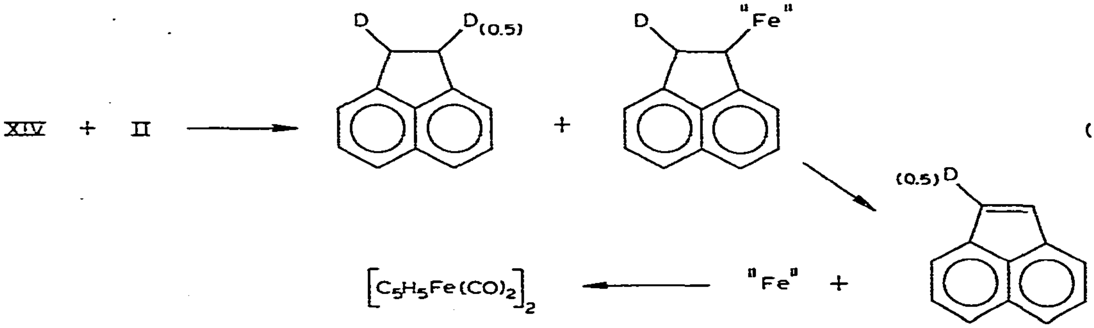
The predominant formation of alkane from the decomposition of I contrasts sharply with the behavior of the $C_5H_5Fe(CO)(PPh_3)(alkyl)$ system in which case alkenes are formed exclusively [6,29]. Since ligand dissociation to give a 16-electron complex should preceed β-elimination, the differences between the two systems may be a reflection of the ease of dissociation of PPh_3 versus CO. There are data available which support the more facile loss of PPh_3. Thus Wojcicki found that treatment of $C_5H_5Fe(CO)(PPh_3)CH_3$ with various phosphites yielded the products of PPh_3 replacement, $C_5H_5Fe(CO)[P(OR)_3]CH_3$ [29]. Furthermore, whereas $C_5H_5Fe(CO)(PPh_3)CH_2CH_3$ gives $C_5H_5Fe(CO)(PPh_3)H$ and ethylene when heated for 30 min in heptane, a process involving reversible phosphine dissociation, $C_5H_5Fe(CO)_2CH_2CH_3$ undergoes migratory insertion to produce $C_5H_5Fe(CO)(PPh_3)COCH_2CH_3$ when treated with PPh_3 rather than suffer CO replacement to give $C_5H_5Fe(CO)(PPh_3)CH_2CH_3$. With ligand dissociation and hence β-elimination from I being relatively difficult, other reaction pathways become accessible. It appears that β-elimination via path (a) does occur to some extent, however, since thermolysis of I under CO did suppress acenaphthylene formation significantly.

Several lines of evidence point to the occurrence of metal—carbon bond homolysis as a major reaction pathway (b). The most obvious of these is the formation of 1,1′-biacenaphthenyl, presumably via coupling of the acenaphthenyl radical (XIV). As Whitesides and coworkers have demonstrated [31], however, the formation of dimeric hydrocarbon products in alkylmetal decompositions in itself does not constitute proof for free radical intermediates. The incorporation of deuterium into the acenaphthene produced from the decomposition of I in toluene-d_8, however, provides a strong indication for the intermediacy of the acenaphthenyl radical. As one might expect for a highly stabilized radical such as XIII, dimerization to IX competes with H-abstraction from solvent. The increased *d*-content in the acenaphthene and decreased *d*-content in the acenaphthylene relative to II is most easily accounted for by disproportion of the acenaphthenyl radical (eq. 19) *. According to Ingold [32], the ratio of



(19)

radical disproportionation to recombination (k_d/k_r) decreases with increasing radical stability. For the 1-phenylethyl radical, which should be a reasonable model for the acenaphthenyl radical, $k_d/k_r = 0.023$ [33]. The relative amount of disproportionation in our system appears to be much greater than expected assuming the change in deuterium content in the products relative to II results only from radical disproportionation and if recombination accounts for about 25% of the characterized products. It is questionable, therefore, whether XIV, if formed, would undergo extensive disproportionation. It is unfortunate that no systematic studies of the acenaphthenyl radical have been published. A similar deuterium distribution would result from β-D (or β-H) abstraction from complex II by the acenaphthenyl radical (eq. 20). Resolution of this question awaits future efforts to generate XIV by alternate means.



(20)

The occurrence of H-abstraction from the cyclopentadienyl ring (path c) is particularly interesting since such reactions are rather uncommon. Previous examples are restricted to complexes of the earlier transition metals, e.g. $(\eta^5\text{-}C_5H_5)_2TiR_2$ [19,20], and actinides, $(\eta^5\text{-}C_5H_5)_3ThR$ [21] and $(\eta^5\text{-}C_5H_5)_3UR$ [22]. The occurrence of Cp—H abstraction in these cases probably is due to suppression of the β-elimination pathway, either from lack of β-hydrogens (in the Ti system) or from difficulty in attaining coordinative unsaturation in the U, Th systems). It would appear that this latter factor is also operating in decomposi-

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* Values shown in parentheses were obtained ignoring isotope effects.

tion of the iron—acenaphthenyl complexes. It is interesting that the analogous benzyl system, (η^5-C_5H_5)Fe(CO)$_2$CH$_2$Ph, apparently doesn't decompose via Cp—H abstraction since no toluene was detected from its thermolysis in n-decane solution [13]. Migration of the benzyl group to the Cp ring, however, was observed as a minor process. This pathway dominates in the thermolyses of $C_5H_5Mo(CO)_3CH_2Ph$ [13], $C_5H_5Mo(CO)_3CH_2CH_3$ [34], $C_5H_5W(CO)_3CH_2Ph$ [13] and $C_5H_5W(CO)_3Ph$ [35]. The markedly different results between the benzyl- and acenaphthenyl-iron systems clearly demonstrate the importance of the alkyl group in influencing the course of the reaction. An explanation for the observed differences, however, is not obvious and must await studies of additional complexes with a variety of alkyl groups. Although it would be premature to speculate as to a mechanism for the Cp—H abstraction process, direct H-abstraction by a free acenaphthenyl radical seems unlikely because of the expected stability of this species.

Experimental

Spectra were obtained on the following instruments: (1) infrared: Beckman IR 10, Perkin—Elmer 137 and 421 spectrometers; (2) mass spectra: Hitachi Perkin—Elmer RMS 4 Mass Spectrometer at 15 eV; (3) NMR spectra: at 60 MHz on Hitachi Perkin—Elmer R-24 and Varian A60A Spectrometers; and (4) ultraviolet-visible; Cary 14 Recording Spectrophotometer or a Hitachi Perkin—Elmer 139 Spectrophotometer. Acenaphthene and acenaphthylene were separated on a 6′ 20% DEGS on Chromosorb W stainless steel column (column A) on a Varian 1700 gas chromatograph. Elemental analyses were performed by Carol K. Fitz, Ph. D., Carlisle, Mass.

Technical grade acenaphthene and acenaphthylene were recrystallized from absolute ethanol. Cyclopentadiene (b.p. 42—44°C) was obtained by cracking dicyclopentadiene at 170°C prior to use. All solvents were reagent grade and were used without further purification. Bis[(cyclopentadienyl)iron dicarbonyl] was prepared as described by King and Stone [36]. [(Cyclopentadienyl)(isobutene)iron dicarbonyl] tetrafluoroborate was prepared by the method of Giering and Rosenblum [37] and [(cyclopentadienyl)(acenaphthylene)iron dicarbonyl]tetrafluoroborate was obtained as reported earlier [30]. Sodium cyanoborodeuteride was prepared according to the method of Borch, Bernstein, and Durst [38]. All manipulations of organometallic compounds were carried out under a nitrogen atmosphere.

Preparation of (cyclopentadienyl)(acenaphthenyl)iron dicarbonyl (I)

A 50 ml three-necked round-bottomed flask equipped with a pressure-equalizing dropping funnel, a gas inlet and a magnetic stirring bar was charged with 0.50 g (1.3 mmol) of [(cyclopentadienyl)(acenaphthylene)iron dicarbonyl]-tetrafluoroborate dissolved in 15 ml of degassed acetonitrile and cooled to 0°C. A solution of 0.10 g (1.5 mmol) of sodium cyanoborohydride in 15 ml of degassed acetonitrile was then added dropwise over a five minute period. After fifteen minutes the solvent was rotary evaporated and the orange residue was extracted with 20 ml portions of degassed petroleum ether (35—55°C) until the extracts were colorless. The combined extracts were filtered through celite and the filtrate was evaporated leaving a yellow-orange oil. The residue was dissolved in a minimum volume of petroleum ether, then admitted to a neutral alumina (act. III) column. Upon development with petroleum ether a highly mobile yellow band was eluted which, upon solvent evaporation, yielded a small quantity of acenaphthylene. Further development produced a slow-moving yellow band which was eluted into a flask cooled at —78°C. Yellow-orange crystals of the product (0.33 g, 77% yield) precipitated; m.p. 71—73°C; IR (CH_2Cl_2): 1985, 1960 cm^{-1} (metal carbonyl); NMR (CS_2): δ 3.30 (m, 1 H), 3.65 (m, 1 H), 3.95 (s(br), 1 H), 4.28 (s, 5 H), 7.25 (m, 6 H) ppm; mass spectrum *m/e* 330 (*P*), 302 (*P* — CO), 274 (*P* — 2 CO). Anal. Found: C, 68.90; H, 4.40. $C_{19}H_{14}FeO_2$ calcd.: C, 69.12; H, 4.27%.

Preparation of (cyclopentadienyl)(trans-2-deuterioacenaphthenyl)iron dicarbonyl (II)

Fifty mg (1.3 mmol) of the acenaphthylene complex V was treated with 0.11 g (1.5 mmol) of sodium cyanoborodeuteride as described above. After extraction with petroleum ether, filtration, and chromatography, 0.32 g (75% yield) of the deuterated complex II was obtained. IR (CH_2Cl_2) 1985, 1960 cm^{-1} (metal carbonyl); NMR (CS_2): δ 3.30 (m, 1 H), 4.05 (s(br), 1 H, $W_{1/2}h = 2$ Hz), 4.30 (s, 5 H), 7.3 (m, 6 H) ppm; mass spectrum *m/e* 331(*P*), 303(*P* — CO), 275(*P* — 2 CO). NMR integration of the aromatic vs. benzylic absorptions indicated 0.9(±0.05) D/molecule.

Preparation of (perdeuteriocyclopentadienyl)(acenaphthenyl)iron dicarbonyl (XIII)

Cyclopentadiene-d_6 was prepared by the method of McLean et al. [39] except for a necessary variation in the workup procedure. After the addition of the sodium deuteroxide solution (0.26 mol of sodium peroxide in 120 ml of 99% deuterium oxide) to 48 g (0.73 mol) of cyclopentadiene in 100 ml of dimethyl sulfoxide, the expected separation into three layers failed to develop. The reaction mixture was then extracted with ten 100 ml portions of low-boiling petroleum ether. The combined extracts were refluxed for three days to induce dimerization of the cyclopentadiene-d_6. The petroleum ether was removed by rotary evaporation and the yellow residual liquid was distilled at 63—66°C/ 12 mmHg to afford 14.5 g (0.098 mol) of dicyclopentadiene-d_{12}.

A 15 ml (0.098 mol) portion of dicyclopentadiene-d_{12} was heated with 9.8 g (0.05 mol) of iron pentacarbonyl according to the method of King and Stone [36] to yield 2.0 g of bis[(perdeuteriocyclopentadienyl)iron dicarbonyl] (X). This material contained approximately 4.0 D/Cp ring as determined by multiple integration of the NMR spectrum of an equimolar mixture of X and naphthalene.

The corresponding [(perdeuteriocyclopentadienyl)(isobutene)iron dicarbonyl]-tetrafluoroborate (XI) was obtained in 38% yield from X according to the procedure for the protio complex.

One gram (3.1 mmol) of the complex XI was heated in 40 ml of 1,2-dichloroethane containing 6.0 g (39 mmol) of acenaphthylene in the usual fashion. After recrystallization from ether/nitromethane, 1.0 g (84% yield) of [(perdeuteriocyclopentadienyl)(acenaphthylene)iron dicarbonyl]tetrafluoroborate (XII) was obtained.

Complex XII was treated with 0.20 g (3.1 mmol) of sodium cyanoborohydride. Workup in the previously described manner gave 0.38 (46%) of (perdeuteriocyclopentadienyl)(acenaphthenyl)iron dicarbonyl (XIII).

General procedure for vacuum thermolyses of (cyclopentadienyl)(acenaphthenyl)-iron dicarbonyl complexes I, II and XIII

The alkyliron (100 mg) was placed in a water-cooled sublimator. The sublimator was evacuated and then immersed in an oil bath at 150°C. The complex rapidly began to decompose, assuming a dark red color. After thirty minutes, the entire decomposition product had sublimed onto the cold finger as a maroon solid. The majority of this material was dissolved in a small amount of pentane and admitted to an alumina (neutral, act III) column. A tan-colored residue which was quite insoluble in both polar and non-polar solvents was not characterized. Development of the column with pentane produced a yellow mobile band which upon elution and solvent evaporation yielded a mixture of acenaphthene and acenaphthylene. The acenaphthene/acenaphthylene ratios for these and other reactions were determined by ultraviolet and NMR spectroscopy (see organic product analysis). Development with 1/1 ether/pentane afforded bis(cyclopentadienyliron dicarbonyl); IR (CH_2Cl_2): 1955, 1940 and 1760 cm^{-1}. Product yields are summarized in Table 1.

Thermolysis of I in the presence of acenaphthylene

An intimate mixture of I (78 mg, 0.24 mmol) and acenaphthylene (37 mg, 0.24 mmol) was heated under vacuum (0.5 mmHg) at 150°C and the volatile products collected on a cold finger. The usual chromatographic workup afforded 63 mg of an acenaphthene/acenaphthylene mixture which was found by spectrophotometric analysis at 370 nm to contain 70% acenaphthylene and 30% acenaphthene. Assuming complete recovery of added acenaphthylene and a 2/1 acenaphthene/acenaphthylene ratio produced from I, the mixture was expected to contain 73% acenaphthylene.

Thermal decomposition of I under carbon monoxide pressure

Complex I (0.10 g, 0.30 mmol) was placed in a stainless steel pressure bomb. The bomb was pressurized with 25 psi of carbon monoxide and then immersed in an oil bath at 150°C for one hour. After opening the vessel, the products were removed by extraction with five 25 ml portions of ether. The combined extracts were rotary evaporated and the red residue treated as previously described. Products yields are presented in Table 1.

Thermolyses of I and II in toluene and toluene-d_8

For those experiments in which determination of the acenaphthene/acenaphthylene ratio was the prime objective the following procedure was employed. A 100 mg (0.30 mmol) sample of the iron complex dissolved in 25 ml of degassed toluene (5 ml. of toluene-d_8) was heated at reflux under nitrogen for 30 min. The toluene was then evaporated at reduced pressure and the residue chromatographed as described in the procedure for vacuum thermolyses. Yields are presented in Table 1 and the acenaphthene/acenaphthylene ratios are given in the text.

TABLE 1

YIELD DATA FOR THERMOLYSES OF ALKYLIRON COMPLEXES

Alkyliron	Thermolysis method	Combined VII + VIII (%)	$[C_5H_5Fe(CO)_2]_2$ (%)
I	V [a]	71	71
I	T [b]	35 [c]	90
I	CO [d]	26	— [f]
I	DT [e]	28	— [f]
II	V	62	62
II	T	41	— [f]
XIII	V	65	75

[a] In vacuo (150°C/0.5 mmHg). [b] Toluene reflux. [c] Biacenaphthenyl (11%) also isolated. [d] Under 2 atm CO. [e] Toluene reflux. [f] Admixed with biacenaphthenyl and polymer.

The $[C_5H_5Fe(CO)_2]_2$ obtained from this workup was contaminated with significant quantities of organic material. A large scale thermolysis and modified workup was used in order to identify this material. Complex I (1.0 g, 3.0 mmol) in 30 ml of degassed toluene was refluxed for 30 min under nitrogen. The toluene was removed by rotary-evaporation and the red residue was extracted with five 2 ml portions of petroleum ether. The combined extracts were transferred to a sublimator, concentrated under a stream of nitrogen, and the residue sublimed at 70°C/0.5 mmHg to afford 0.16 g (35%) of an acenaphthene/acenaphthylene mixture. The non-volatile residue was combined with the petroleum ether-insoluble material and chromatographed over silica gel/benzene. A mobile yellow-orange band eluted first with benzene and was concentrated to give 0.22 g of an orange oil. Continued development with benzene eluted a burgundy band which yielded 0.48 g (90%) of $[C_5H_5Fe(CO)_2]_2$ identified by its IR and NMR spectra. Rechromatography of the orange oil on silica gel yielded 0.10 g of pale yellow solid upon development with 1/4 benzene/petroleum ether. The material was identified as a mixture of *meso-* and *d,l*-1,1′-biacenaphthenyl (m.p. 114—120°C, lit. [40] 124 and 168°C). ^1H NMR (CS_2): δ 6.6—7.7 (m, 12 H), 4.5 (m, 2 H), and 2.7—3.8 ppm (m, 4 H); *m/e* 306(*P*), 153($\frac{1}{2}P$). Development with pure benzene afforded 0.06 g of unidentified yellow solid: ^1H NMR (CS_2): δ 6.8—8.0 (m(br)), 3.0—4.2 m(br) ppm.

Assessment of the deuterium content from the labeling experiments carried out in solution is described in the organic product analysis section.

Organic product analysis

The yellow band first eluted upon chromatography was shown to be a mixture of acenaphthene (VII) and acenaphthylene (VIII) by comparison of the PMR spectrum of the mixture with authentic samples. This was further verified by GC separation of VII and VIII; these had PMR spectra and melting points identical to authentic samples.

For those experiments in which neither the alkyliron nor the solvent were deuterium enriched, the amounts of acenaphthene and acenaphthylene were determined independently by visible and PMR spectroscopic methods, neither of which required that they be separated. The amount of each component in the mixture was determined by PMR in CS_2 by comparison of the average integrated values (at least five-repetitions) of the benzylic protons of VII (δ 3.2 ppm) and the olefinic protons of VIII (δ 6.8 ppm). Analysis by visible spectroscopy was carried out at 370 nm. At this wavelength acenaphthylene absorbs significantly whereas acenaphthene is essentially transparent. Since standard acenaphthene/acenaphthylene mixtures exhibited good Beer's law behavior in the 10^{-3} M concentration range, the amount of acenaphthylene and hence acenaphthene present in an unknown mixture was determined directly by measuring the absorbance of 4.0×10^{-3} M cyclohexane solutions of the mixtures. Values obtained by the two spectroscopic methods agreed within ±3% in all cases.

In the deuterium labeling experiments acenaphthene/acenaphthylene ratios were determined by visible spectroscopy as described above or by comparison of the relative peak areas obtained from gas chromatography on Column A.

In order to determine the deuterium content of VII and VIII the product mixtures were first separated by preparative GC comparison of multiple NMR integrations in the acenaphthenes, or aromatic vs. benzylic absorptions, and in the acenaphthylenes, of aromatic vs. olefinic absorptions yielded the average number of deuteriums incorporated into each acenaphthene and acenaphthylene molecule.

Acknowledgment

Acknowledgment is made to the Research Corporation and to the Donors of the Petroleum Research Fund, administered by the American Chemical Society, for the support of this research. We also thank Dr. George Vogel for obtaining the mass spectra.

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