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Chemistry of 2-Naphthyl Bis[bis(dimethylphosphino)ethane] Hydride Complexes of Iron, Ruthenium, and Osmium. 3. Cleavage of sp^2 C–H Bonds

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Abstract: Reactions of HMNp(dmpe)$_2$ complexes (Np = 2-naphthyl; dmpe = $Me_2PCH_2CH_2PMe_2$; M = Fe or Ru) to cleave various sp^2 C–H bonds, including those of aromatic hydrocarbons, are described. The new HMR(dmpe)$_2$ complexes are characterized spectroscopically. Studies of substituted benzenes show that product stability is favored by electron-withdrawing substituents and inhibited by electron donors. By a combination of NMR spectroscopy, specific deuterium labeling, and disubstitution, it has been possible to establish which isomeric products are formed. The overall study of HMNp(dmpe)$_2$ chemistry is summarized, and the factors favoring C–H bond cleavage by low-valent transition metals are discussed.

Introduction

The first reports of the activation of C–H bonds by soluble transition metal complexes appeared in 1963 and 1965. These reactions[1,2] (eq 1 and 2) provide examples of both *intra-* and *inter*molecular C–H bond cleavage at sp^2 carbon atoms (Np = 2-naphthyl; dmpe = $Me_2PCH_2CH_2PMe_2$). Subsequently,

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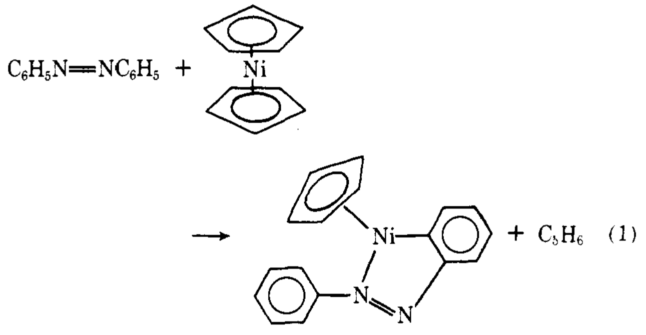

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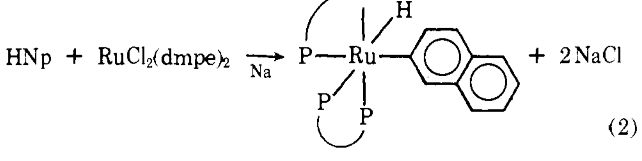
(1)



(2)

cis-2b

there have been related reports,[3] many involving intramolecular reactions in complexes containing bulky phosphines. *Catalytic* H-D exchange between D_2 and mono- or disubstituted benzenes has been studied.[4] Competitive exchange experiments using $H_3Nb(\pi\text{-}C_5H_5)_2$ as catalyst show relative rates increased in the order $p\text{-}(CH_3)_2 \ll CH_3 \sim OCH_3 < H < CF_3 \sim F < p\text{-}F_2$. A mechanism involving a series of reductive-elimination and oxidative-addition steps was proposed, but *no* aryl hydride intermediates were actually observed. $HM(C_6H_4R)(\pi\text{-}C_5H_5)_2$ (M = Mo or W; R = H or CH_3) have been obtained from $M(\pi\text{-}C_5H_5)_2$ intermediates generated chemically or photolytically.[5]

Ethylene and benzene react with $Os_3(CO)_{12}$ to give isolable $H_2Os_3(CO)_9(CH_2C)$ and $H_2Os_3(CO)_9(C_6H_4)$ complexes formed by cleavage of *two* sp^2 C-H bonds. The X-ray structure of the former compound has been determined.[6] These reactions do, however, require rather forcing conditions: 24 h in refluxing octane (125 °C) and 2 days at 194 °C, respectively. Cleavage of one C-H bond of ethylene to give $HOs_3(CO)_{10}(CH{=}CH_2)$ can be effected under much milder conditions (40 h at 25 °C) using the coordinatively unsaturated cluster $H_2Os_3(CO)_{10}$.[7] Labeling studies indicate that the two hydrogen atoms present initially do not appear in the product but reduce 1 mol of ethylene to ethane. Other olefins (propylene, 1-hexene, isobutylene, and styrene) give similar $HOs_3(CO)_{10}(CH{=}CHR)$ products in reactions with the intermediate $[Os_3(CO)_{10}]$, produced by reductive elimination of diethyl succinate on gentle heating (25-50 °C) of $HOs_3(CO)_{10}[CH(COOEt)\text{-}CH_2COOEt]$.[8] Aromatic C-H bonds are not, however, activated under these conditions.

In this paper we describe the spectroscopic characterization of various complexes $HMR(dmpe)_2$ (M = Fe or Ru) formed in the substitution reaction

$$HMNp(dmpe)_2 + HR \rightleftharpoons HMR(dmpe)_2 + HNp \quad (3)$$

by cleavage of aromatic and other sp^2 C-H bonds under mild conditions (a few hours at 25 °C). Because these complexes are easily formed, particularly with M = Fe, the product stabilities and structures were investigated in detail. Earlier papers described the characterization of the $HMNp(dmpe)_2$ complexes[9] [M = Fe (**2a**), Ru (**2b**), or Os (**2c**)] and their reactions to cleave sp and sp^3 C-H bonds, as well as C-O and C-halogen bonds.[10] In this paper, we also summarize the entire study and compare the behavior of the three types of C-H bonds in terms of the resulting metal-carbon bonds. A preliminary account of our work has already been published.[11]

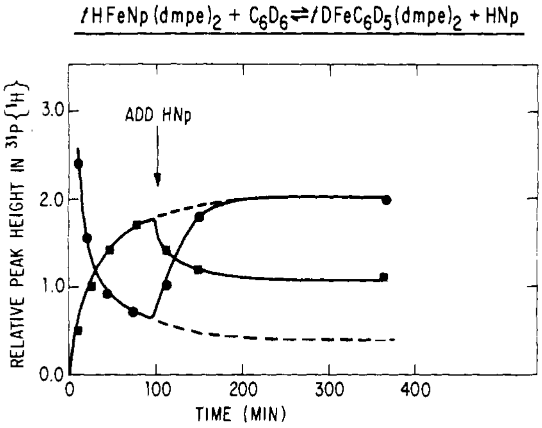


Figure 1. $^{31}P\{^1H\}$ NMR peak heights of *trans*-$HFeNp(dmpe)_2$ (●, singlet at −74.2 ppm) and *trans*-$DFeC_6D_5(dmpe)_2$ (■, 1:1:1 triplet at −74.7 ppm) relative to internal *trans*-$FeCl_2(dmpe)_2$ (singlet at −58.3 ppm) after dissolving 0.1 mmol of $HFeNp(dmpe)_2$ in 1.8 mL of C_6D_6 (21 mmol) at ambient temperature. The dashed line is for a run with no additions, the solid line for a run in which 1.0 mmol of naphthylene was added after 100 min.

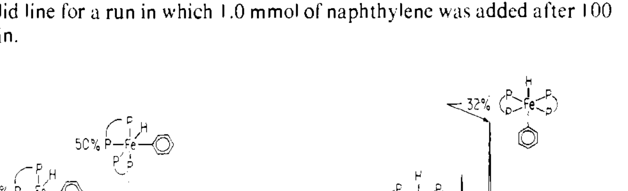


Figure 2. The hydride region of the 100-MHz ^1H NMR spectrum 1 day after dissolving 0.1 mmol of $HFeNp(dmpe)_2$ in 0.3 mL of C_6H_6 + 0.3 mL of C_6D_6.

Results

It is convenient to divide the reactions investigated into categories depending on the type of reactive bonds which the substrates contain: (1) unsubstituted aromatic compounds, (2) substituted benzenes, and (3) nonaromatic sp^2 C-H bonds.

Unsubstituted Aromatic Compounds. When $HFeNp(dmpe)_2$ (**2a**) is dissolved in C_6D_6, a reaction occurs in which naphthylene in the cis-trans mixture of naphthyl hydrides is replaced by deuteriobenzene. The strong singlet of *trans*-**2a** at −74.2 ppm in the $^{31}P\{^1H\}$ spectrum[9] loses intensity and a new 1:1:1 triplet (J_{PD} = 7.5 Hz) grows in at −74.7 ppm. The pattern results from coupling of the equivalent ^{31}P nuclei with D in *trans*-$DFeC_6D_5(dmpe)_2$. The ABCD pattern of *cis*-**2a** is simultaneously obscured by the unresolved resonances of *cis*-$DFeC_6D_5(dmpe)_2$ at nearly the same chemical shifts, implying a relatively rapid cis-trans equilibration. Figure 1 shows the results of experiments in which the peak heights of *trans*-**2a** and *trans*-$DFeC_6D_5(dmpe)_2$ were followed with time. In the absence of added HNp, the heights followed the dashed curves. Addition of HNp reversed the equation

$$HFeNp(dmpe)_2 + C_6D_6 \rightleftharpoons DFeC_6D_5(dmpe)_2 + HNp \quad (4)$$

From the relative peak heights of the trans complexes at equilibrium a value of K_4 = 0.08 is determined at ambient temperature, indicating a greater affinity for naphthylene relative to benzene by a factor of about 12. The half-life of the reaction is about 20 min.

Figure 2 shows the hydride region ^1H NMR spectrum after equilibrating $HFeNp(dmpe)_2$ in a 50/50 mixture of C_6H_6/

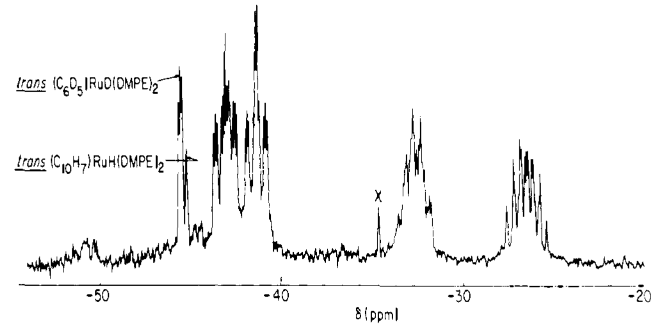


Figure 3. The $^{31}P\{^1H\}$ NMR spectrum of a solution initially containing 0.1 mmol of *cis*-HRuNp(dmpe)$_2$ in 1.8 mL of C_6D_6, after heating for 36 h at 60 °C. The weak pattern at −51 ppm is the A-wing line of the tightly coupled AB part of the ABCD spectrum. X marks an impurity.

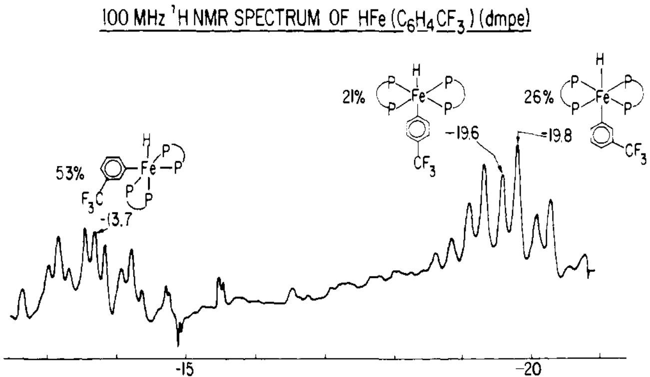


Figure 4. The hydride region of the 100-MHz ^1H NMR spectrum of HFe($C_6H_4CF_3$)(dmpe)$_2$ isomers in C_6D_6.

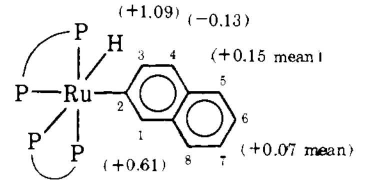
C_6D_6. The stronger hydride resonances centered at −13.4 and −19.7 ppm are due to *cis*- and *trans*-HFeC_6H_5(dmpe)$_2$,[12] respectively, in a 3:2 concentration ratio. Weaker resonances at −13.3 (shoulders) and −19.5 ppm are due to unreacted *cis*- and *trans*-HFeNp(dmpe)$_2$. The relative peak heights of *trans*-HFeC_6H_5(dmpe)$_2$ and *trans*-HFeNp(dmpe)$_2$ are in good agreement with those calculated from K_4 = 0.08. An experiment in which the reaction of HFeNp(dmpe)$_2$ with 50/50 C_6H_6/C_6D_6 was followed with time by $^{31}P\{^1H\}$ NMR did not show a measurable isotope effect—a not surprising result for rate-determining loss of HNp. There was also no isotope effect when the mixture was allowed to react with CH_3CN; this experiment did show, however, that reductive elimination of benzene is considerably faster than that of naphthylene.

HRuNp(dmpe)$_2$ (**2b**) reacts with C_6D_6 much more slowly than does **2a.** Little or no reaction is detectable after standing at ambient temperature for 4 days. Heating for 18 h at 60 °C gives a mixture of *cis*- and *trans*-**2b** and *cis*- and *trans*-DRuC_6D_5(dmpe)$_2$, which changes only slightly on further heating. Figure 3 shows the resulting $^{31}P\{^1H\}$ spectrum, in which the P-D coupling in *cis*-DRuC_6D_5(dmpe)$_2$ is clearly resolved. The largest deuterium coupling is found with P_D, consistent with a trans arrangement of D and P_D. The phosphorus at highest field in *cis*-**2b** was shown earlier[9] to be trans to H by selective $^1H\{^{31}P\}$ decoupling experiments.

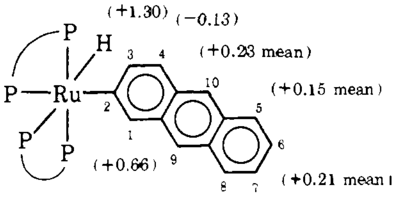
No reaction of HOsNp(dmpe)$_2$ (**2c**) with C_6D_6 was detected after a solution (which also contained CH_3CN) was heated for 60 h at 75 °C; the complex merely isomerized from nearly all *cis*-**2c** to an isomeric mixture containing 25% *trans*-**2c.**[10]

The complex **2a**-d_8 was prepared[9] by sodium naphthylenide-d_8 reduction of $FeCl_2$(dmpe)$_2$. It can also be prepared by adding $C_{10}D_8$ to a THF solution of **2a,** as shown by the appearance of the characteristic 1:1:1 triplet in the $^{31}P\{^1H\}$ NMR spectrum.

Anthracene reacts with **2a** to give an unusual η^4-1,3-diene-like complex ($C_{14}H_{10}$)Fe(dmpe)$_2$, in which one dmpe is monodentate and one bidentate.[9] With **2b,** however, anthracene gives the more usual C-H bond cleavage product, HRu($C_{14}H_9$)(dmpe)$_2$; structure **3** follows from the ABCD pattern in the $^{31}P\{^1H\}$ NMR spectrum, the hydride resonances in the ^1H NMR spectrum, and the assignment of the nine unique aromatic proton resonances, which are resolved at 220 MHz. The assignment can be made from the multiplet patterns by analogy with *cis*-**2b**;[9] the coordination chemical shifts $\Delta\delta$ (in parentheses on the structures shown) for the two compounds can be seen to be very similar for protons similarly situated with respect to Ru. Note the large downfield shifts of the ortho protons. The actual chemical shifts for **3** are given in Table I; we cannot distinguish between protons H_6 and H_7, H_5 and H_8, or H_9 and H_{10}, for which the chemical shifts within a pair differ by less than 0.1 ppm.



cis-**2b**



3

The different pathways for reactions with anthracene taken by iron and ruthenium suggest that the 1,3-diene structure is more stable thermodynamically than the anthryl hydride for Fe, but that the reverse is true for Ru. $^{31}P\{^1H\}$ NMR experiments in which the formation of ($C_{14}H_{10}$)Fe(dmpe)$_2$ was followed with time gave no indication of formation of an anthryl hydride complex. It is well-known that iron has a propensity for forming η^4-1,3-diene complexes and that anthracene is more diene-like than naphthalene, but this is nonetheless a remarkable selectivity.

Phenanthrene reacts with **2a** to give a mixture of products. A singlet at −74.1 ppm in the $^{31}P\{^1H\}$ NMR spectrum suggests[13] that the phenanthryl Fe(II) hydride is present. Another resonance at −61.7 ppm remains unidentified but seems to arise from a zerovalent species.[13] Phenanthrene is much less reactive than anthracene; resonances of DFeC_6D_5(dmpe)$_2$ and **2a** persisted in a solution containing a tenfold excess of phenanthrene to iron.

Substituted Benzenes. There are six possible isomeric aryl metal hydrides which might be produced in the cleavage of aromatic C-H bonds of a monosubstituted benzene. The C-H cleavage could occur ortho, meta, or para to the substituent, and the resulting M-C and M-H bonds could be cis or trans to each other on the metal. With benzotrifluoride, fluorobenzene, and toluene, we have unambiguously assigned the product structures by a combination of NMR, deuterium labeling, and disubstitution.

Figure 4 shows a hydride NMR spectrum obtained on equilibrating **2a** with $C_6H_5CF_3$ in C_6D_6. The resonance at δ −13.7 is a cis aryl hydride pattern while the quintets near −20 ppm show two trans aryl hydride complexes. The $^{31}P\{^1H\}$ NMR spectrum confirms their presence and further shows that DFeC_6D_5(dmpe)$_2$ and **2a** are no longer present. The position of Fe on the ring in each complex is established by the hydride

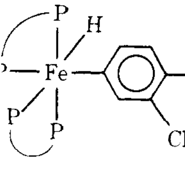
Table I. ^{31}P and ^{1}H NMR Data[a] for $HMR(dmpe)_2$ Complexes (R = Aryl)

complex[b]	^{31}P NMR	^{1}H NMR hydride	^{1}H NMR other[c]
trans-$HFeC_6H_4F$ (**5**)	−75.8 d (9),[d] −73.8 s	−20.7 dq (51, 7)[d]	
trans-$HFeC_6H_3F_2$ (**6**)	−75.2 br	−20.8 dq (50.5, 6.5)[d]	7.11 dt (11.5, 3), 6.60, 6.58 t (8)
cis-$HFeC_6H_3F_2$	*e*	−12.5 br	7.45 br, 6.77, 6.80 t (8)
trans-$HFeC_5H_4N$ (**18-20**)	−74.8, −74.2, −73.4 s	−18.4 qu (46), −19.2 qu (48), −19.5 qu (48.5)	
cis-$HFeC_5H_4N$	*e*	−13.8[f]	
trans-$HFeC_6H_5$	−74.5[g]	−19.7 qu (48.5)	
cis-$HFeC_6H_5$	*e*	−13.4 m (68, 53, 53, 38)[h]	
trans-$HFeC_6H_4CH_3$ (**7, 8**)	−74.4, −74.3 s		
cis-$HFeC_6H_4CH_3$	*e*		
trans-$HFeC_6H_4COOC_2H_5$	−74.2, −73.5 s	−19.1 qu (48), −19.6 qu (50)	
cis-$HFeC_6H_4COOC_2H_5$	*e*	−13.6 m (66, 52, 52, 38)[h]	
trans-$HFeC_6H_4COOCH_3$	−74.1, −73.5 s	−18.6 qu (48), −19.2 qu (48)	3.64, 3.60 s
cis-$HFeC_6H_4COOCH_3$	*e*	−13.6 m (66, 52, 52, 38)	
trans-$HFeC_6H_4OCH_3$ (**11**)	−74.1 s[i]		
trans-$HFeC_6H_4Cl$	−73.7 s[i]		
trans-$HFeC_6H_4CF_3$	−73.5 br[j]	−19.6 qu (49), −19.8 qu (48.5)	
cis-$HFeC_6H_4CF_3$		−13.7 m (68, 53, 53, 38)[h]	
trans-$HFeC_6H_4CN$ (**16, 17**)	−73.0. −72.6 s	−19.2 qu (49), −19.8 qu (49)	
cis-$HFeC_6H_4CN$ (**13a**)	*k*	−12.2 dddd (71, 52, 46, 40)	8.20 d (7.5), 7.35 t (7.5)
cis-$HFeC_6H_4CN$ (**14, 15**)	*e*	−13.7 m (67,52, 52, 38)[h]	
cis-$HFeC_6H_3(CH_3)CN$ (**13b**)	*k*	−12.2 dddd (71, 54, 46, 39)	8.08 d (7), 7.50 d (7)
trans-$HFeC_6H_3(CF_3)_2$ (**4**)	−72.7 s	−19.4 qu (49)	7.94 br s, 7.43 br d (7.5), 7.08 d (7.5)
cis-$HFeC_6H_3(CF_3)_2$	*l*	−13.8 m (66, 32, 52, 38)[h]	
trans-$HFeC_6H_4COCH_3$	−70.0, −69.8 s	−18.9 qu (48), −19.6 qu (50)	2.87, 2.37 s
cis-$HFeC_6H_4COCH_3$	*e*	−13.5 m (66, 52, 52, 38)[h]	
trans-$DRuC_6D_5$	−45.6 t (3.5)		
cis-$DRuC_6D_5$	*m*		
trans-$HRuC_{14}H_9$	−45.3 s		
cis- $HRuC_{14}H_9$ (**3**)	*e*	−8.9 dq (89, 24)	*n*
trans-$HRuC_6H_4CN$	−45.3 s	−18.2 qu (22)	
cis-$HRuC_6H_4CN$	*e*	−8.1, −8.4, −8.8 dq (4)	

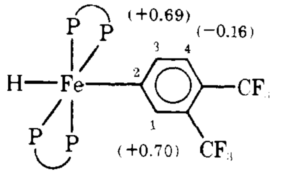
[a] In C_6D_6. Chemical shifts are in parts per million, negative downfield from external 85% H_3PO_4 for ^{31}P and positive downfield from internal tetramethylsilane for ^{1}H. Coupling constants (in parentheses) are in hertz. Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet; br, broad. dq (51, 7) means a doublet of quartets with a doublet splitting of 51 Hz and quartet splitting of 7 Hz. [b] The two dmpe ligands present in each complex are omitted for clarity. [c] Resonances other than those of dmpe. [d] Couplings <10 Hz are due to ^{19}F. [e] An unresolved ABCD pattern. [f] An unresolved mixture of isomers. [g] C_6D_6 gives a 1:1:1 triplet at −74.7 ppm with $J_{PD} = 7.5$ Hz. [h] A multiplet with the intensity pattern 1/1:2:1/2:2:2/1:2:1/1. [i] Transient aryl hydride goes to more stable nonhydride products. [j] A high-field shoulder indicates the presence of two trans isomers. [k] Under low resolution, the spectrum looks like an A_2B_2 pattern with δ_A −68.2, δ_B −59.2, $J_{AB} = 40$ Hz. See Figure 7. [l] An ABCD pattern with δ_A −73.0, δ_B −67.2, δ_C −58.7, δ_D −51.3; $J_{AB} = 95$, $J_{AC} = 24$, $J_{AD} = J_{BC} = 32$, $J_{BD} = J_{CD} = 16$ Hz. [m] Chemical shifts (and P-D coupling constants): −44.8 (3.5), −39.8 (3.5), −32.8 (3.5), and −26.6 (14.0). $J_{AB} = 273$ Hz. See Figure 3. [n] H_3, 8.55 d (8) br; H_1, 8.46 d (5) br; $H_{9,10}$, 8.40, 8.37 s; $H_{5,8}$, 8.00, 7.91 d (8); H_4, 7.67 d (8); $H_{6,7}$, 7.52, 7.40 t (8). There was very little trans isomer (by ^{31}P).

NMR spectra of the selectively deuterated benzotrifluoride complexes. p-$CF_3C_6H_4D$ gives a spectrum similar to that of Figure 4 except that the quintet at −19.6 ppm is missing. m-$CF_3C_6H_4D$ gives a spectrum in which the resonance at −19.6 ppm is unaffected while those at −13.7 and −19.8 ppm are reduced in intensity by about a factor of 2. These results establish the assignment shown in Figure 4. The absence of a resonance assignable to *cis*-$HFe(p\text{-}C_6H_4CF_3)(dmpe)_2$ suggests a low concentration and/or a coincidence with the multiplet at −13.7 ppm. The absence of isomers with Fe ortho to CF_3 is undoubtedly steric in origin; space-filling models support this conclusion.

o-$C_6H_4(CF_3)_2$ reacts with **2a** to give one cis (~40%) and one trans(~60%) aryl hydride product. Structure *trans*-**4** (Δδ in parentheses) follows from the assignment of the aromatic region in the ^{1}H NMR spectrum. Note the similarity of coordination chemical shifts with those in **3**. Actual chemical shifts and coupling constants are given in Table I. Protons $H_{1,4}$ (δ 7.24) and $H_{2,3}$ (6.70) in the unreacted substrate can be distinguished by the large H-F coupling of the ortho protons. (Both coupling constants are <1 Hz.) Protons H_1 and H_3 in *trans*-**4** show additional broadening due to unresolved H-P coupling.

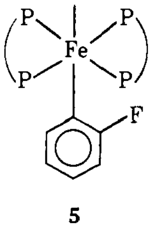


cis-**4**



trans-**4**

Fluorobenzene and **2a** at equilibrium give only *one* aryl hydride, assigned structure **5** on the following basis. The hydride NMR spectrum shows a quintet, further split into a doublet with $J_{HF} = 7$ Hz. The $^{31}P\{^{1}H\}$ NMR spectrum shows a strong doublet with $J_{PF} = 8$ Hz. Very similar ^{1}H hydride and ^{31}P NMR spectra are shown by complexes prepared from p-FC_6H_4D, m-FC_6H_4D, or p-$C_6H_4F_2$. The last must have structure **6**.



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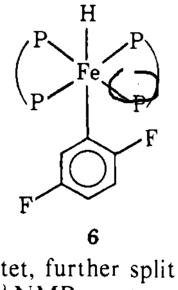

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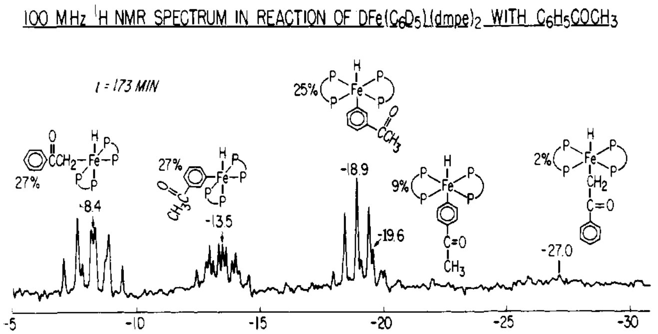


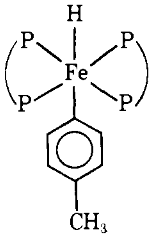
Figure 5. The hydride region 100-MHz ^1H NMR spectrum of a solution initially containing 0.1 mmol of $HFeNp(dmpe)_2$ and 0.15 mmol of acetophenone in C_6D_6, run 173 min after mixing.

Table II. Selected IR Stretching Frequencies[a]

complex	ν_{MH}[b]	ν_{CO} or ν_{CN}	$\Delta\nu$[c]
$HFeC_6H_4COOC_2H_5$		1694	−22
$HFeC_6H_4CN$		2211 (2195)[d]	−12 (−38)[d]
$HFeC_6H_3(CH_3)CN$		2193	−40
$HFeC_6H_4COCH_3$	1790	1643 (1555)[e]	−41 (−129)[e]
$HFeCOC_6H_5$		1504	−198
$HFeCH{=}C(CH_3)$-$COOC_2H_5$	1810	1658	−57
$HRuC_6H_4CN$	1820	2210, 2200	−17, −27

[a] cm^{-1} in C_6D_6. [b] These bands were broad and weak when observed. [c] The change in ν_{CO} or ν_{CN} on complex formation. [d] Values in parentheses are for an isomer with Fe ortho to -CN. [e] Values in parentheses are for the $HFeCH_2COC_6H_5$ isomer.

Toluene has a potentially reactive CH_3 group in addition to the ortho, meta, and para ring protons. The $^{31}P\{^1H\}$ NMR spectrum of **2a** in toluene shows two singlet resonances around −73 ppm, in addition to one assigned to *trans*-$HFeNp(dmpe)_2$. These have a 1:1.6 intensity ratio and become 1:1:1 triplets if toluene-d_8 is used as the solvent.[14] Selective deuterium labeling experiments show that the weaker downfield resonance is due to **7** while the stronger one at slightly higher field is due to **8.**



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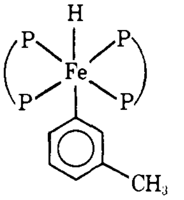

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There is no evidence for isomers with Fe ortho to the methyl group, or for cleavage of methyl C–H bonds. We attribute the absence of ortho attack to a steric effect. Correcting for statistical effects, Fe has a slight preference for the para C–H bond over the meta (1.0:0.8). From the relative intensities in the $^{31}P\{^1H\}$ NMR spectrum of a solution of **2a** in a 50/50 mixture of toluene and C_6D_6, we can estimate a value of K_5 of 0.17. (This includes meta and para isomers of the trans tolyl hydrides.)

$$\textit{trans}\text{-}DFeC_6D_5(dmpe)_2 + C_6H_5CH_3 \overset{K_5}{\rightleftharpoons} \textit{trans}\text{-}HFeC_6H_4CH_3(dmpe)_2 + C_6D_6 \quad (5)$$

After correcting for statistical effects, it is found that the para C–H bond of toluene is only 0.4 times as reactive as the C–D bond of benzene.

Our conclusions about steric control of the isomer distribution in methyl-substituted benzenes is supported by attempted reactions with *p*-xylene and mesitylene; **2a** dissolves in these solvents with no reaction. Green found that photochemically generated $(\pi\text{-}C_5H_5)_2W$ reacted with toluene to give a *p*-tolyl tungsten hydride analogous to **7** as the major product.[5b] His intermediate did, however, react with methyl groups of *p*-xylene and mesitylene to give $(\pi\text{-}C_5H_5)_2$-$W(CH_2Ar)_2$ products.[15]

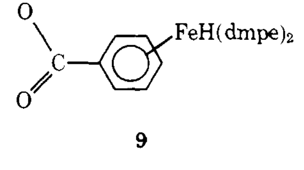
The acetophenone C–H bonds show the effect of carbonyl activation of the phenyl and methyl groups. The reaction of **2a** with a small excess of acetophenone in C_6D_6 was followed with time by repeatedly running the hydride region ^1H NMR spectrum. Figure 5 shows such a spectrum 173 min after mixing. Resonances at δ −13.5, −18.9, and −19.6 ppm are assigned as shown on the basis of analogy with the patterns and relative intensities of the benzotrifluoride adduct. A parallel time-dependent $^{31}P\{^1H\}$ NMR experiment showed that little **2a** was still present after this time. The strong doublet of quartets at −8.4 ppm has nearly the same chemical shift and coupling constants as *cis*-$HFe(CH_2COCH_3)(dmpe)_2$,[10] and is assigned to *cis*-$HFe(CH_2COC_6H_5)(dmpe)_2$. A very weak quintet at −27.0 ppm which is barely visible in Figure 5, but which grew in intensity in later spectra, has nearly the same chemical shift as the trans acetone adduct.[10] To assure attainment of equilibrium, spectra were taken up to 1600 min after mixing. Following the reaction of acetophenone with time showed that (1) cleavage of aromatic sp^2 C–H bonds is more rapid than of the sp^3 C–H bonds, (2) products of sp^3 bond cleavage are, however, slightly more stable, and (3) isomerization among aryl hydride isomers (both cis–trans and positional) is relatively fast, while isomerization of the alkyl hydride isomers is relatively slow. The slow isomerization of *cis*- to *trans*-$HFe(CH_2CN)(dmpe)_2$ was described earlier.[10]

That acetophenone competes effectively with C_6D_6, even with the latter present in large excess, shows that the carbonyl group strongly activates both the ring and methyl hydrogens. Comparison with toluene indicates that the methyl group is more strongly activated. The carbonyl is, of course, closer to these C–H bonds.

The infrared spectrum of the above solution showed bands at 1643 (m) and 1555 (s) cm^{-1} assigned to the $HFeC_6H_4COCH_3$ and $HFeCH_2COC_6H_5$ isomers, respectively. The band at lower energy (Table II) is assigned to the $HFeCH_2COC_6H_5$ isomer by analogy with $HFeCH_2COCH_3$.[10]

The hydride region ^1H NMR spectrum after the reaction of ethyl benzoate with **2a** looks much like Figure 4, indicating exclusive attack on the ring hydrogens at the meta and para positions. NMR data are given in Table I. The presence of some $DFe(C_6D_5)(dmpe)_2$ in the final $^{31}P\{^1H\}$ NMR spectrum indicates that, while the -COOEt substituent strongly activates the ring, the effect is not as great as with $-CF_3$ or $-COCH_3$. The infrared spectrum shows a medium-intensity band assigned to ν_{CO} (22 cm^{-1} lower in frequency than free ethyl benzoate).

Reaction with methyl benzoate gives an analogous product, $HFe(C_6H_4COOCH_3)(dmpe)_2$ (**9**), with similar spectral properties. The major product of the reaction, however, is **10,** arising from cleavage of the ester C–O bond.[10] We ascribe the



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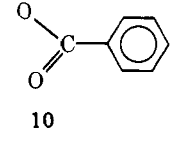

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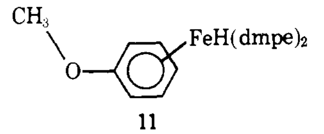
difference in behavior between ethyl and methyl esters to the reduced steric crowding in the methyl iron complex, but it may also reflect the greater susceptibility of methyl to nucleophilic attack.

Since the methyl group in toluene deactivates the ring hydrogens, it might be anticipated that the methoxy group would be even more strongly deactivating. In an experiment where $^{31}P\{^1H\}$ NMR spectra were recorded at various times after dissolving **2a** in a 50/50 mixture of $C_6D_6/C_6H_5OCH_3$, a transient shoulder was observed at −74.1 ppm assigned to **11.** On standing, however, the more stable isomer **12** formed, giving a $^{31}P\{^1H\}$ NMR singlet at −69.4 ppm.[10]



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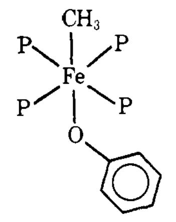

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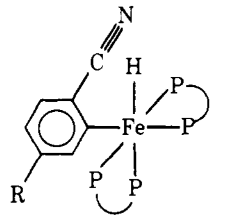
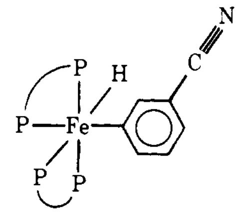
Chlorobenzene also gave a transitory aryl hydride intermediate ($^{31}P\{^1H\}$ NMR singlet at −73.7 ppm). A final product peak at −68.4 ppm is assigned to *trans*-$C_6H_5FeCl(dmpe)_2$. Another peak at −58.3 ppm is assigned to *trans*-$FeCl_2(dmpe)_2$.[9] There were no hydride resonances in the ^1H NMR spectrum at the end of the reaction. Photochemically generated $(\pi\text{-}C_5H_5)_2W$ also reacts with chlorobenzene, giving $(\pi\text{-}C_5H_5)_2W(C_6H_5)Cl$.[5a]

Benzonitrile reacts with **2a** to give a mixture of at least four aryl hydride complexes, as shown by the hydride region ^1H NMR spectrum in Figure 6a. The unusual 16-line pattern at −12.2 ppm is assigned to **13a.** This is supported by the spectrum of the *p*-tolunitrile reaction product (**13b**) in Figure 6b, where *only* this pattern is observed. Positions meta and para to the cyano group are blocked by the methyl in *p*-tolunitrile. Molecular models show that complexes with iron ortho to cyano are possible only with the Fe-H and Fe-C bonds cis to each other, and with the cyano group oriented as shown in **13.** The other resonances in Figure 6a are assigned as shown, along with the percentages of isomers as determined from the hydride intensities. The more conventional looking cis aryl hydride multiplet at −13.7 ppm could be a superposition of **14** and **15.** Infrared spectra show two bands of coordinated benzonitrile at 2211 and 2195 cm^{-1}. The lower frequency is assigned to the *o*-CN isomer **13a** on the basis that only one band at 2193 cm^{-1} is found for **13b.** The $^{31}P\{^1H\}$ NMR spectra of **13a** (Figure 7) and **13b** are similar, showing what looks like a broadened A_2B_2 pattern. Figure 7 also shows two singlets due to the trans isomers **16** and **17.** There is no evidence for methyl C-H cleavage with *p*-tolunitrile.



13a, R = H
b, R = CH_3



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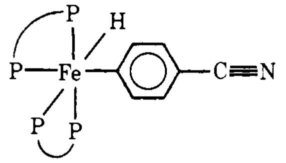

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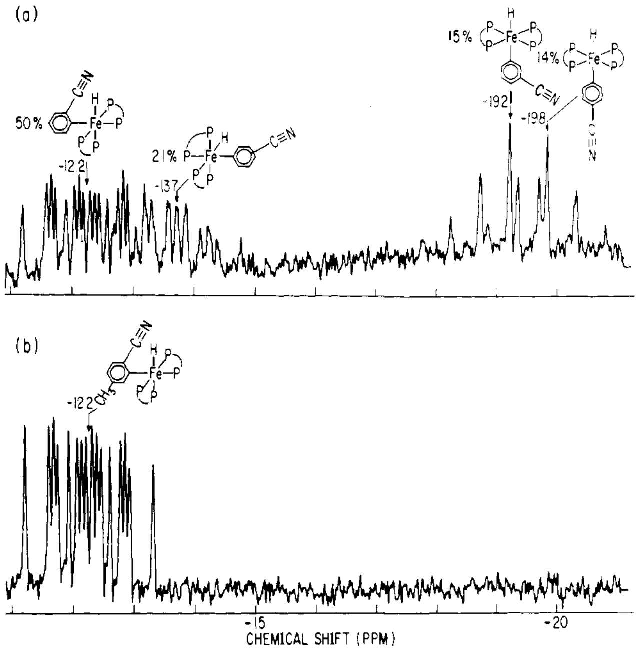


Figure 6. The hydride region 100-MHz ^1H NMR spectra produced by the reactions of $HFeNp(dmpe)_2$ in C_6D_6 with (a) benzonitrile and (b) *p*-tolunitrile.

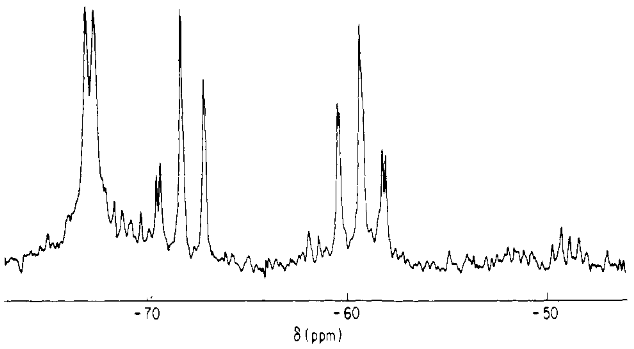
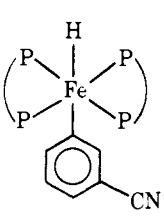


Figure 7. The $^{31}P\{^1H\}$ NMR spectrum of $HFe(C_6H_4CN)(dmpe)_2$ isomers in C_6D_6.



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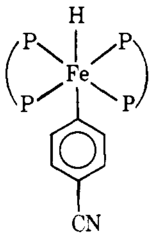

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The reaction of benzonitrile with **2b** gives a product with a more conventional spacing of the ABCD $^{31}P\{^1H\}$ multiplets; the hydride NMR spectrum shows three doublets of quartets and one weaker quintet, indicating the presence of three cis isomers (ortho, meta, and para) and one trans.

Pyridine reacts with cleavage of C-H bonds, although it has the potential to behave as a Lewis base and form a five-coordinate Fe(0) complex. The hydride region ^1H NMR spectrum shows a mixture of cis and trans isomers. Though the complex cis multiplets centered at δ −13.8 ppm were not resolved, three trans quintets were observed at −18.4, −19.2, and −19.5 ppm with relative intensities of 56:34:10, respectively. While we believe that these may be assigned to the ortho (**18**), meta (**19**), and para (**20**) trans isomers, respectively, no attempt was made

Table III. ^{31}P and ^{1}H NMR Data[a] for $HFeR(dmpe)_2$ Complexes (R = Acyl or Vinyl)

complex	^{31}P NMR	^{1}H NMR	
		hydride	other
cis-$HFeCOC_6H_5$ (**21**)	*b*	−12.3 dq (33, 52)	
cis-$HFeCOC_2H_5$	*c*	−12.7 dq (34, 52)	
cis-$HFeCH{=}C(CH_3)COOC_2H_5$ (**23**)	*d*	−12.9 dq (42, 55)	10.15 brd (23), 4.30 dq (1.6, 7.2) 2.77 t (2.5), 1.21 t (7.2)

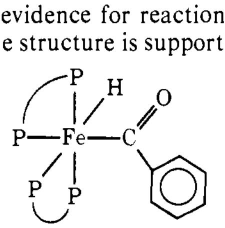
[a] The same chemical shift conventions and abbreviations are used as in Table I. [b] An ABCD pattern with $\delta_A \sim -68.4$ dd, $\delta_B \sim -65.9$ t, δ_C −59.1 ddd, and δ_D −55.1 ddd; $J_{AC} = 33$, $J_{AD} = 16$, $J_{BC} = 24$, $J_{BD} = 25$, $J_{CD} = 9$ Hz. δ_A, δ_B, and J_{AB} could not be accurately determined because the wing lines of the tightly coupled A and B were so weak. [c] An unresolved ABCD pattern with chemical shifts similar to **21**. [d] An incompletely resolved ABCD pattern with δ_A −76.8 dt (89, 31), $\delta_B \sim -69$ m, $\delta_C \sim -61$ m, and δ_D −57.1 m.

to confirm the assignment by substitution. The $^{31}P\{^1H\}$ NMR spectrum shows that pyridine forms much more stable aryl hydrides than does benzene; no $DFeC_6D_5(dmpe)_2$ was detected in a solution containing 0.15 mmol of pyridine and 20 mmol of C_6D_6.

Benzonitrile and pyridine might have acted as Lewis bases to form five-coordinate Fe(0) compounds. That they did not shows the greater stability of the aryl hydride complexes. While small phosphorus ligands (L) give $LFe(dmpe)_2$, PPh_3 is so bulky that it reacts instead as a substituted benzene.[16] In this respect it acts like $HCPh_3$.[10]

Nitrobenzene, unlike other substituted benzenes, reacts with **2a** immediately upon mixing. The resulting deep violet solution shows new $^{31}P\{^1H\}$ NMR resonances attributable to oxidized dmpe. The remaining iron is apparently oxidized to paramagnetic species. A similar reaction was observed with nitromethane.[10]

Nonaromatic sp^2 C–H Bonds. Benzaldehyde reacts with **2a** to give **21**, with no evidence for reaction with the aromatic hydrogen atoms. The structure is supported by loss of the aldehyde ^1H NMR resonance at δ 9.66 ppm, by the new hydride doublet of quartets at −12.3 ppm, and by the ABCD $^{31}P\{^1H\}$ NMR pattern.[17] An infrared band at 1504 cm^{-1}, 198 cm^{-1} lower than free benzaldehyde, is assigned to ν_{CO} in **21**. The compound does not lose benzene to form $(CO)Fe(dmpe)_2$ even on standing at room temperature for 1 month. The complex is the type of intermediate one would expect on a reaction pathway coupling benzene and CO. In our system, however, reaction of $HFeC_6H_5(dmpe)_2$ with CO gives only benzene and $(CO)Fe(dmpe)_2$,[9] probably the more thermodynamically stable products. The kinetic stability of these products precludes a more detailed analysis.



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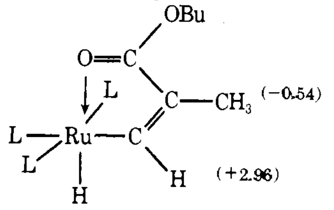
Propionaldehyde reacts with **2a**, in a manner analogous to that with benzaldehyde, to give *cis*-$HFe(COC_2H_5)(dmpe)_2$, with a hydride resonance (Table III) very similar to that of **21**. In this case, however, further reactions take place. After the initial formation of the acyl complex, $(CO)Fe(dmpe)_2$, identified by its $^{31}P\{^1H\}$ NMR and infrared spectra, begins to form at the expense of the acyl hydride. Other unidentified complexes were also formed. Acyl hydrides have been proposed as intermediates in the decarbonylation of aldehydes by $RhCl(PPh_3)_3$,[18a] but rarely observed.[18b]

Following the report of Yamamoto, Ibers, and co-workers[19] that the reaction of butyl methacrylate with $H_2Ru(PPh_3)_4$ gives **22** [L = PPh_3; the numbers are the changes in δ (ppm) upon coordination)],[19,20] we investigated the reaction of ethyl methacrylate with **2a**. The spectral data are consistent with structure **23**. The doublet of quartets for the hydride resonance (Table III) indicates C–H cleavage to give a cis complex. The protons of the ethoxycarbonylpropenyl ligand can be observed in the ^1H NMR spectrum with the correct integrated intensities, and with the coordination chemical shifts (Δδ) shown. Particularly unusual is the vinylic proton at δ = 10.15 ppm, which appears as a broad doublet with J_{PH} = 23 Hz; the unusually large coupling suggests close proximity to one of the phosphorus atoms; other couplings are not resolved. The vinylic CH_3 in **23** is shifted to lower field, and appears as a broadened triplet (J_{wings} = 5 Hz). It is because of this, and the positive Δδ, that we draw **23** with the Fe and CH_3 cis with respect to the double bond. The vinylic CH_3 Δδ in **22** is negative and is known to be trans to Ru from the X-ray crystal structure.[19] A trans geometry about the double bond is favored in **22** because it permits the ester carbonyl group to coordinate, reducing its stretching frequency by 140 cm^{-1}.[19] A lack of coordination of the ester carbonyl in **23** is indicated by a much smaller change in $\nu_{C=O}$ (−57 cm^{-1}, Table II). Molecular models suggest that isomer **23** has less steric crowding than one with the Fe and ester group cis.



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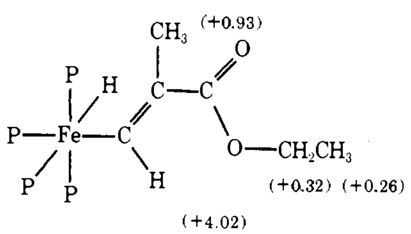
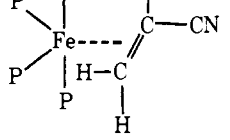


23

Unexpectedly, methacrylonitrile reacts with **2a** to form a π-bonded olefin complex **24**.[9] The different structures of **23** and **24** indicate that rather subtle factors determine whether C–H cleavage or olefin complex formation occurs. It is interesting that styrene in our system gives an olefin complex,[9] whereas Shapley[8] observed vinyl C–H cleavage on an osmium cluster.



24

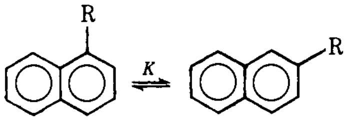
Discussion

The work we have described in this paper and the preceding[9,10,21] papers shows that oxidative addition of C–H bonds to low-valent transition metal complexes is favored by coordinative unsaturation and a high electron density at the metal center. The reductive elimination of naphthalene from $HFeNp(dmpe)_2$ provides a four-coordinate, zerovalent intermediate which meets both of these criteria. The reactivity sequence **2a** ≫ **2b** ≫ **2c** is a consequence of decreasing rates of reductive elimination going down the triad.

Coordinative unsaturation also accounts for the reactivity of $[(\pi\text{-}C_5H_5)_2W]$ and $[(\pi\text{-}C_5H_5)_2Mo]$.[5] The importance of coordinative unsaturation in clusters is indicated by the much greater reactivity of $H_2Os_3(CO)_{10}$[7] compared to $Os_3(CO)_{12}$.[6] A feature of clusters (and metal surfaces), not possible in mononuclear complexes, is for one metal atom to hold a substrate (e.g., C_2H_4 by the π electrons) while an adjacent one breaks a C-H bond. This probably occurs in the reaction of C_2H_4 with $[Os_3(CO)_{10}]$.[7] It has an analogy with intramolecular C-H cleavage in mononuclear complexes where a C-H bond of an organic ligand (possibly bound to the metal by P) is held in close proximity to the metal atom.

The importance of a high electron density on the metal is indicated by the lack of reactivity in C-H cleavage of many known unsaturated complexes with less basicity, and by comparison of the results on the $M(dmpe)_2$ complexes with those recently obtained on the isoelectronic $Fe(dppe)_2$[21] (dppe = $Ph_2PCH_2CH_2PPh_2$) and cationic Rh(I) and Ir(I) analogues. $Fe(dppe)_2$, generated from a variety of precursors, reacts with terminal acetylenes and HCN to give isolable $HFeR(dppe)_2$ species. Reactions with activated methylene compounds give other hydrido species through disproportionation reactions, but the only aromatic C-H bond cleavage observed is the intramolecular ortho metalation with one of the dppe phenyl rings. $Ir(dmpe)_2^+$ reacts with terminal acetylenes, nitromethane, acetonitrile, and acetone to give complexes of the type $HIrR(dmpe)_2^+$ but does not react with benzene.[22] Reduction of $RuCl_2(PPh_3)_4$ in CH_3CN was thought to give $(\pi\text{-}CH_3CN)Ru(PPh_3)_4{\cdot}CH_3CN$[23a] rather than a $HRuCH_2CN$ complex. This complex is now formulated as an ortho-metalated triphenylphosphine species.[23b]

Cleavage of C-H bonds also depends on the structure of the organic substrate. It is clear that both steric and electronic effects are involved. The exclusive formation of 2-naphthyl hydrides with the $M(dmpe)_2$ fragment is a consequence of the large steric requirements of $HM(dmpe)_2$. Olah[24] has reported equilibrium constants for eq 6, which increase monotonically



(6)

in the sequence R = Me < Et < *i*-Pr < *t*-Bu. With R = *t*-Bu, the 1-naphthyl isomer is undetectable. Space-filling molecular models show that $HM(dmpe)_2$ has appreciably greater steric bulk than *t*-Bu. Steric factors also explain why toluene, trifluorobenzene, acetophenone, and alkyl benzoates show no products in which $HM(dmpe)_2$ is ortho to the substituents, while pyridine, fluorobenzene, and benzonitrile do display ortho C-H cleavage.

Steric effects also explain why sp^2 C-H bonds are broken in $HC(C_6H_5)_3$ and fluorene, while an sp^3 bond is preferred in cyclopentadiene. The large cone angle[25] of 145° for $P(C_6H_5)_3$ dictates C-H cleavage rather than the Lewis base adduct formation preferred by smaller phosphines. Subtle steric differences appear to explain why methyl benzoate reacts with cleavage of a C-O bond, while ethyl benzoate does not, and why ethyl methacrylate gives a vinyl hydride while methacrylonitrile forms an olefin complex.

Steric effects are generally assumed to produce kinetic control of product mixtures; in these reactions, however, the product mixtures reported appear to be thermodynamic. This is in contrast to the previous work on aromatic C-H activation (H-D exchange) in which the product mixtures were clearly kinetic in origin.[3,4] Many of the reactions reported here were followed with time (as in Figure 5) until there was no further change.

Table IV. Strengths[a] of C-H Bonds toward Homolytic Cleavage

compd	bond type	D(R-H), kcal/mol
HCN	sp	129
C_6H_5-H, C_2H_3-H	sp^2	104
C_2H_5-H	sp^3	98
CH_3COCH_2-H		92
$NCCH_2$-H		86
$C_6H_5CH_2$-H, $CH_2{=}CHCH_2$—H		85

[a] Taken from J. A. Kerr, *Chem. Rev.*, **66**, 465 (1966).

The possibility of a very stable thermodynamic product (such as an alkyl hydride from toluene) which is not formed for kinetic reasons seems unlikely because, as already noted, the formation of all $Fe(dmpe)_2$ complexes, whether zerovalent Lewis base adducts or divalent hydrido species, takes place on approximately the same time scale (a matter of hours at 25 °C). The rate-limiting step is H-R reductive elimination and the subsequent H-R oxidative addition is extremely fast.

Electronic factors are also extremely important. The lack of reactivity of pentane, the reaction of aromatic rather than aliphatic C-H bonds in toluene, and reaction of the acetylenic hydrogen of phenylacetylene show that, in the absence of special activating effects (or steric inhibition), the reactivity of C-H bonds decreases in the sequence $sp > sp^2 > sp^3$. This is opposite to what would be expected on the basis of the homolytic C-H bond strengths shown in Table IV, and indicates that the strengths of the M-C bonds in the same order ($sp \gg sp^2 \gg sp^3$) more than make up for the energy required to break the stronger C-H bonds. This is probably a consequence of the overlap of metal orbitals with carbon p orbitals, particularly important with M—C≡C but also significant with M—aryl. The strength of the M—C≡C interaction can be inferred from the 80-cm^{-1} reduction in $\nu_{C\equiv C}$ on C—H cleavage of acetylene, or the -42-cm^{-1} $\Delta\nu_{C\equiv N}$ for HCN.[10]

The complexity of the product mixtures makes it difficult to measure accurate equilibrium constants for competition between substrates for C-H cleavage. It is clear, nevertheless, that electron-withdrawing substituents on the organic substrate favor C-H cleavage and that the effect is large. For example, no $DFe(C_6D_5)(dmpe)_2$ can be observed in a solution containing initially 0.1 mmol of Fe and 0.15 mmol of benzotrifluoride in 20 mmol of C_6D_6, so that a lower limit of 4×10^3 can be set on K_7.[26]

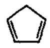
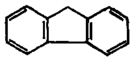
$$DFe(C_6D_5)(dmpe)_2 + C_6H_5CF_3 \overset{K_7}{\rightleftharpoons} HFe(C_6H_4CF_3)(dmpe)_2 + C_6D_6 \quad (7)$$

Statistical correction for the accessibility of only three positions of benzotrifluoride gives a reactivity per C-H bond $>10^4$ times greater in $C_6H_5CF_3$ than in C_6H_6.

Electronegative groups have an even stronger effect on sp^3 C-H bonds if the group is attached to the carbon in question, as was shown in the case of acetophenone. The effectiveness of such groups must lie in their ability to drain off electron density from the carbon attached to the metal. The importance of this effect is indicated by the large $\Delta\nu_{C\equiv N}$ (-90 cm^{-1}) in *trans*-$HFeCH_2CN(dmpe)_2$,[10] and suggests that the R groups in $HFeR(dmpe)_2$ complexes have substantial carbanionic character. This helps to rationalize the preferential reaction at the methylene in phenylacetone and cyclopentadiene.[10]

Carbanion stability alone does not explain why toluene reacts at a ring rather than at a methyl C-H,[27] nor why ace-

Table V. Strengths of Carbon Acids

compd	pK_a[a]	D(R-H) − EA(R),[b] kcal/mol
HCN	9	
CH_3NO_2	11	
$NCCH_2CN$	12	17.2
	15	39.1
$HC{\equiv}CC_6H_5$	18	
$CH_3COC_6H_5$	19	45.6
CH_3COCH_3	20	50.4
$CH_3SO_2CH_3$	23	
	23	34.9
$HC{\equiv}CH$	25	
CH_3CN	25	52.7
$HC(C_6H_5)_3$	33	
$HCH_2C_6H_5$	35	37.0
C_6H_6, C_2H_4	37	
C_2H_6	42	

[a] D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965. [b] Values in the gas phase, from ref 28. D(R-H) is the energy for homolytic cleavage of the R-H bond and EA(R) is the electron affinity of R·.

tonitrile gives a more stable adduct than acetone. The carbanion pK_a values in Table V refer to the equation

$$HR \overset{K_a}{\rightleftharpoons} H^+ + R^- \qquad (8)$$

in protonic solvents, usually H_2O.[28] Recent work on the acidities of carbon acids in the gas phase, using a pulsed electron beam mass spectrometer technique, shows that the ordering of acidities in solution can be strongly influenced by solvation effects, particularly in the case of small anions.[29] The quantity D(R-H) − EA(R) in Table V is the ΔH[30] for

$$e^- + RH \rightarrow H\cdot + R^- \qquad (9)$$

A larger value corresponds to a weaker acid. Though the gas-phase acidities seem more appropriate for our reactions, which were usually run in solvents whose solvation properties are expected to be small, they predict that toluene should give a more stable adduct than acetonitrile, a result clearly at variance with the facts. The weakness of the carbanion idea is that it ignores the metal-carbon bond. If one thinks of the C-H cleavage as occurring in four parts:

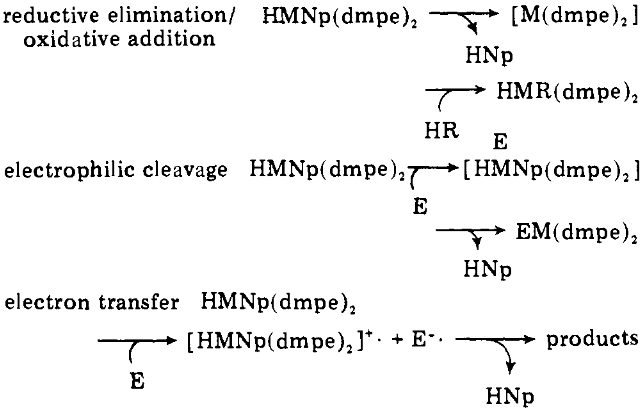
$$\begin{array}{rlr}
R\text{-}H \rightarrow H\cdot + R\cdot & D(R\text{-}H) & (10) \\
H\cdot + R\cdot \rightarrow H^+ + R^- & IP(H) - EA(R) & (11) \\
H^+ + M \rightarrow HM^+ & \text{constant} & (12) \\
HM^+ + R^- \rightarrow HMR & & (13) \\
\hline
RH + M \rightarrow HMR & \Delta H & (14)
\end{array}$$

the important role of the M-R bond strength (where M represents the metal and ancillary ligands) along with D(R-H) and EA(R), can be seen. This scheme is not meant to imply that there is no change in metal-ligand or M-H bond strengths as R changes. Quite the contrary, an unfavorable steric interaction may weaken not only the M-R bond but also the other metal-ligand bonds. All of these effects would be summed into eq 14.

We now consider briefly the mechanisms of reactions of the HMNp(dmpe)$_2$ complexes. Most of the C-H cleavage reactions (and all of the Lewis base ligand additions) go by a mechanism involving reductive elimination of naphthylene as a rate-determining step. This was demonstrated explicitly by the kinetic studies on the reaction of CH_3CN[10] (and CO)[9] with **2a** and probably in other reactions of **2a** which proceed at similar rates.

A major exception to this rule is the reaction with HCN, which must occur by electrophilic attack since the reaction is complete upon mixing, even with the normally sluggish HRuNp(dmpe)$_2$. HCN is the strongest carbon acid we have studied. Nitromethane, the second strongest carbon acid in Table V, causes immediate destruction of **2a** and oxidation of the dmpe ligands. Electrophilic attack is also indicated for HCl, and is supported by the observation of Chatt and Davidson that treatment of HRuNp(dmpe)$_2$ with DCl gives naphthalene-d_1.[2] As Kochi has recently pointed out, there is a continuum of mechanisms between electrophilic attack and electron transfer, depending on the extent to which electrons are actually transferred from the organometallic reagent to the oxidant. In his work these extremes are represented by the reactions of dialkyl mercurials with acetic acid[31] on the one hand and with $IrCl_6^{3-}$ on the other.[32] In both cases the reaction rates correlate well with the photoelectron (UV PES) gas-phase ionization potentials, which range from 9.3 eV for $HgMe_2$ to 7.6 eV for Hg(t-Bu)$_2$.[32] In our system, the rapid reactions with TCNE or CH_3NO_2 are likely examples of electron transfer. The three mechanisms are shown in Scheme I.

Scheme I



Though we do not know the ionization potentials of the HMNp(dmpe)$_2$ complexes, the UV photoelectron spectrum values for (π-C_5H_5)$_2$WH_2 and (π-C_5H_5)MoH_2, which cleave a variety of C-H bonds after loss of H_2,[5] are only 6.4 eV.[33] The lower frequency of ν_{CO} in (CO)Fe(dmpe)$_2$ (1812 cm^{-1})[9] relative to (π-C_5H_5)$_2$W(CO) (1864 cm^{-1})[34] suggests that the ionization potential of HFeNp(dmpe)$_2$ will be even less. Low ionization potentials will probably be a general feature of transition-metal complexes capable of facile C-H bond cleavage. This will of necessity mean that they will also be highly susceptible to electrophilic attack.

Experimental Section

All manipulations were carried out in the dry nitrogen atmosphere of a Vacuum Atmospheres drybox. All solvents were dried by standard techniques. Melting points were measured under nitrogen and are uncorrected. The meta and para d_1 derivatives of toluene, fluorobenzene, and benzotrifluoride were prepared from the appropriate monobromo derivatives by D_2O hydrolysis of the Grignard reagents. The preparation of HFeNp(dmpe)$_2$ has been described previously.[9] All other reactants, perdeuterio reactants, and toluene-d_3 were commercially available. The $^{31}P\{^1H\}$ NMR spectra were recorded in the FT mode on a Bruker HFX-90 spectrometer at 36.43 MHz. Proton spectra were recorded in the CW mode on Varian HR-220 and XL-100 spectrometers. The signal/noise of 100-MHz hydride region NMR spectra were enhanced by collecting 20 CW scans on a Varian C1024 time-averaging computer. Analyses were carried out in our analytical facilities.

Preparation of *trans*-HFe(*o*-C_6H_4F)(dmpe)$_2$. A solution of HFeNp(dmpe)$_2$ (0.48 g, 1.0 mmol) in tetrahydrofuran (20 mL) was treated with an excess of fluorobenzene (0.19 mL, 0.19 g, 2 mmol). The mixture was stirred overnight with little color change. The solution was filtered to remove suspended solids and the solvent was removed under vacuum. Naphthylene was removed by sublimation. The entire process was repeated and the resultant solids were recrystallized from ether, collected by vacuum filtration, and dried under vacuum, yield 50%, mp 139 °C. Anal. Calcd for $FeP_4C_{18}H_{37}F$: C, 47.8; H, 8.26. Found: C, 47.2; H, 8.23.

Preparation of *cis*-HFe(*o*-NCC_6H_3Me)(dmpe)$_2$. The reaction was carried out in a manner analogous to the previous reaction, using *p*-tolunitrile (0.22 g, 2 mmol). The mixture turned red-brown, yield 60%, mp 178 °C. Anal. Calcd for $FeP_4C_{20}H_{39}N$: C, 50.8; H, 8.3; N, 3.0. Found: C, 51.1; H, 8.1, N, 2.9.

Spectroscopic data are given in Tables I and II.

Microscale Reactions. Typically 0.1 mmol of HMNp(dmpe)$_2$ in a small test tube was treated with 0.15 mmol of reactant in 0.8 mL of C_6D_6. Reaction mixtures of iron complexes allowed to proceed overnight at room temperature were usually filtered to remove solid precipitates before running ^1H NMR spectra. For ^{31}P NMR spectra the same solutions were washed into 10-mm tubes with 1 mL of fresh solvent. IR spectra were usually run on these solutions or after stripping the NMR solvent and redissolving the residue in THF. Some reactions were followed as a function of time to assure that equilibrium had been obtained. These reactions were normally monitored at intervals such as soon after mixing, 30, 60, and 90 min, 2, 4, 8, 24, and sometimes 48 h. Reaction mixtures with HRuNp(dmpe)$_2$ were usually heated at 60 °C to speed reaction and in these cases it is not clear that equilibrium was achieved.

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(13) Though −74.1 ppm is essentially the same as $\delta(^{31}P)$ of *trans*-HFeNp(dmpe)$_2$, we can confidently assign it to *trans*-HFeAn(dmpe)$_2$ (An = anthryl) because its intensity increased significantly when the amount of phenanthrene in a solution containing 0.1 mmol of Fe was increased from 0.2 to 1.0 mmol. The value −61.7 ppm is close to the bidentate dmpe resonance in the anthracene Fe(0) complex at −63.4 ppm.
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