

- (51) Y. Saito, J. Takemoto, B. Hutchinson, and K. Nakamoto, *Inorg. Chem.*, **11**, 2003 (1972).  
 (52) In fact for  $\text{Co}(\text{CN})_6^{3-}$  a large Stokes shift corresponding to an increase of 0.10 Å in the metal-carbon equilibrium distance of 1.89 Å has been observed.<sup>53</sup> On this basis we predict that the excited-state  $\text{Co}(\text{CN})_6^{4-}$

- \*  $\text{Co}(\text{CN})_6^{3-}$  exchange reaction should proceed  $\sim 10^5$  times faster than the corresponding ground-state exchange reaction.  
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## The Chemistry of 2-Naphthyl Bis[bis(dimethylphosphino)ethane] Hydride Complexes of Fe, Ru, and Os. 2. Cleavage of sp and sp<sup>3</sup> C-H, C-O, and C-X Bonds. Coupling of Carbon Dioxide and Acetonitrile

S. D. Ittel,\* C. A. Tolman,\* A. D. English, and J. P. Jesson

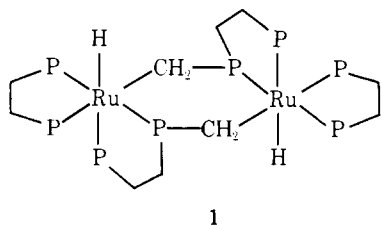
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**Abstract:** Reactions of  $\text{HMNp}(\text{dmpe})_2$  (Np = 2-naphthyl, dmpe =  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ , M = Fe, Ru, or Os) with HCN, terminal acetylenes, and molecules having activated sp<sup>3</sup> C-H bonds to give new  $\text{HMR}(\text{dmpe})_2$  complexes are described. A major factor determining the stability of the products appears to be the stability of the carbanion  $\text{R}^-$ . Rate studies indicate two distinct mechanisms: (1) rapid direct electrophilic attack on the naphthyl hydride, observed with HCN, and (2) slow, rate-determining reductive elimination of naphthylene (rate constant  $k_1$ ), followed by rapid oxidative addition of RH to the 16-electron intermediate  $[\text{M}(\text{dmpe})_2]$ . Kinetic studies on the reaction of  $\text{CH}_3\text{CN}$  with  $\text{HFeNp}(\text{dmpe})_2$  in THF give  $k_1 = 0.022 \pm 0.003 \text{ min}^{-1}$  at 25 °C and  $0.10 \pm 0.1 \text{ min}^{-1}$  at 40 °C. Initial formation of *cis*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$ , followed by slow isomerization to the more stable *trans* isomer is consistent with a three-center transition state for the oxidative addition. Coupling of acetonitrile and  $\text{CO}_2$  as a route to methyl cyanoacetate has been demonstrated. Reactions of the naphthyl hydrides with some esters and ethers to cleave C-O bonds, and with alkyl and aryl halides to cleave C-X bonds, are also described.

### Introduction

Because of the potential importance of selective reactions of hydrocarbons under mild conditions, there has been a rapidly growing interest in the activation of C-H bonds by transition metal complexes.<sup>1</sup> Many examples of *intramolecular*<sup>2</sup> metallation reactions are known. *Intermolecular*<sup>2</sup> reactions to cleave C-H bonds are much more rare, particularly those cases where the HMC adduct has sufficient stability to be isolated or characterized spectroscopically; oxidative additions of the sp C-H bond of  $\text{HCN}^3$  or of terminal acetylenes<sup>3d,4</sup> are the best known. Recent examples of intermolecular cleavage of sp<sup>3</sup> C-H bonds include the reactions of photolytically generate  $(\pi\text{-C}_5\text{H}_5)_2\text{W}$  with *p*-xylene or mesitylene to give  $(\pi\text{-C}_5\text{H}_5)_2\text{W}(\text{CH}_2\text{Ar})_2$  complexes,<sup>5</sup> and of (cyclohexyne)- $\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)$  with  $\text{CH}_3\text{NO}_2$ ,  $\text{CH}_3\text{COCH}_3$ ,  $\text{CH}_3\text{COPh}$ , or  $\text{NCCH}_2\text{Ph}$  to give (cyclohexenyl) $\text{PtR}(\text{diphos})$ .<sup>6</sup> Acetonitrile adds to certain  $\text{IrL}_4^+$  complexes [ $\text{L}_4 = (\text{PMe}_3)_4$  or  $(\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2)_2$ ] to give complexes of the type  $\text{HIr}(\text{CH}_2\text{CN})\text{L}_4^+$ .<sup>7</sup>

Compound **1**, formed in the pyrolysis of  $\text{HRuNp}(\text{dmpe})_2^8$  [dmpe =  $\text{Me}_2\text{PCH}_2\text{CH}_2\text{PMe}_2$ , Np = 2-naphthyl], was prob-



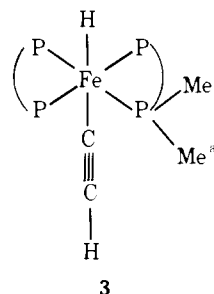
ably the first example of an intermolecular sp<sup>3</sup> C-H cleavage, though that fact was not recognized until an X-ray structure<sup>9</sup> was carried out at a later date.

In the preceding paper<sup>10</sup> we have described the spectroscopic characterization of the  $\text{HMNp}(\text{dmpe})_2$  complexes [M = Fe

(**2a**), Ru (**2b**), or Os (**2c**)] in solution and their reactions with H<sub>2</sub> and various Lewis base ligands. The spectroscopic properties of the products—particularly the exceptionally low  $\nu_{\text{CO}}$  frequency (1812 cm<sup>-1</sup>) in  $(\text{CO})\text{Fe}(\text{dmpe})_2$  and the high-field shift ( $\delta$  0.6 ppm) of the ethylenic protons in  $(\text{C}_2\text{H}_4)\text{-Fe}(\text{dmpe})_2$ —indicate a very high electron density on the  $\text{Fe}(\text{dmpe})_2$  fragment. In this paper the implications of this high electron density for cleavage of C-H bonds having sp or sp<sup>3</sup> hybridization at carbon are explored. Cleavage of C-O and C-halogen bonds is also described. Rate studies show two distinct types of oxidative addition mechanisms: direct electrophilic attack on  $\text{HMNp}(\text{dmpe})_2$ , and oxidative addition to intermediate  $[\text{M}(\text{dmpe})_2]$  formed by a rate-determining reductive elimination of naphthylene. The coupling of acetonitrile and  $\text{CO}_2$  to give cyanoacetic acid is also described. A succeeding paper<sup>11</sup> in this series will deal with reactions of sp<sup>2</sup> C-H bonds. Some of the results described in the present paper have been reported briefly.<sup>12</sup>

### Results and Discussion

**Cleavage of sp C-H Bonds.** As described earlier,<sup>10</sup> diphenylacetylene reacts with **2a** to form a  $\pi$ -bonded acetylene complex. In contrast, acetylene itself reacts with cleavage of the sp C-H bond to form the hydridoacetylide complex **3**. The



**Table I.**  $^{31}\text{P}$  and  $^1\text{H}$  NMR Data<sup>a</sup> for  $\text{HMR}(\text{dmpe})_2$  Complexes Where R = Acetylide or Cyanide

complex	$^{31}\text{P}$ NMR <sup>b</sup>	$^1\text{H}$ NMR <sup>c</sup>		
		hydride	dmpe Me	other
<i>trans</i> - $\text{HFeC}_2\text{H}(\text{dmpe})_2$ ( <b>3</b> )	-73.5 s	-18.31 qu (45)	1.56, 1.16 br s	1.77 qu (2.5)
<i>trans</i> - $\text{HFeC}_2\text{Ph}(\text{dmpe})_2$	-73.9 s	-17.76 qu (45)	1.48, 1.16 br s	7.5-6.7 m
<i>trans</i> - $\text{HFeC}_2$ - <i>t</i> -Bu( $\text{dmpe})_2$	-74.1 s	-18.61 qu (45)		1.38 s
<i>trans</i> - $\text{HFeCN}(\text{dmpe})_2$ ( <b>4a</b> )	-73.8 s	-18.29 qu (46)	1.47, 1.02 br s	
<i>trans</i> - $\text{HRuCN}(\text{dmpe})_2$ ( <b>4b</b> )	-43.4 s	-12.70 qu (21.5)	1.45, 1.13 br s	
<i>cis</i> - $\text{HRuCN}(\text{dmpe})_2$	<i>d</i>	-9.21 dq (82, 24)		
<i>trans</i> - $\text{HOsCN}(\text{dmpe})_2$ ( <b>4c</b> )	- 3.6 s	-13.5 qu (18)	1.50, 1.27 br s	
<i>cis</i> - $\text{HOsCN}(\text{dmpe})_2$	<i>e</i>	-10.72 dq (59, 20)		

<sup>a</sup> In  $\text{C}_6\text{D}_6$ . Abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; qu, quintet; m, multiplet; br, broad. <sup>b</sup>Chemical shifts in parts per million (negative downfield) from external 85%  $\text{H}_3\text{PO}_4$ . <sup>c</sup> Chemical shifts in parts per million (positive downfield) from internal  $\text{Me}_4\text{Si}$ . Values of  $J_{\text{PH}}$  in parentheses in hertz. When there are two numbers in parentheses, the first refers to  $J_{\text{PH}}$  *trans*. <sup>d</sup> The solution contained about 15% *cis* isomer. <sup>e</sup> After heating for 18 h at 60 °C the  $^1\text{H}$  spectrum showed ~30% *cis* isomer; a  $^{31}\text{P}$  spectrum was not recorded at this point. Further heating for 60 h at 75 °C caused complete conversion to the *trans* isomer.

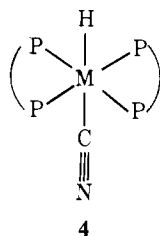
**Table II.** IR Stretching Frequencies<sup>a</sup> in  $\text{HMR}(\text{dmpe})_2$  Where R = Acetylide or Cyanide

complex	$\nu_{\text{MH}}$	$\nu_{\text{C}\equiv\text{N}}$ or $\nu_{\text{C}\equiv\text{C}}$	$-\Delta\nu^b$
<i>trans</i> - $\text{HFeC}_2\text{H}(\text{dmpe})_2$ ( <b>3</b> )	1725	1894	80 <sup>c</sup>
<i>trans</i> - $\text{HFeC}_2\text{Ph}(\text{dmpe})_2$	1720	2036	74
<i>trans</i> - $\text{HFeC}_2$ - <i>t</i> -Bu- ( $\text{dmpe})_2$	1730	2060	
<i>trans</i> - $\text{HFeCN}(\text{dmpe})_2$ ( <b>4a</b> )	1750	2043	42
$\text{HRuCN}(\text{dmpe})_2^d$	1790	2082, 2062	24
$\text{HOsCN}(\text{dmpe})_2^d$	1865	2020, 2055	31

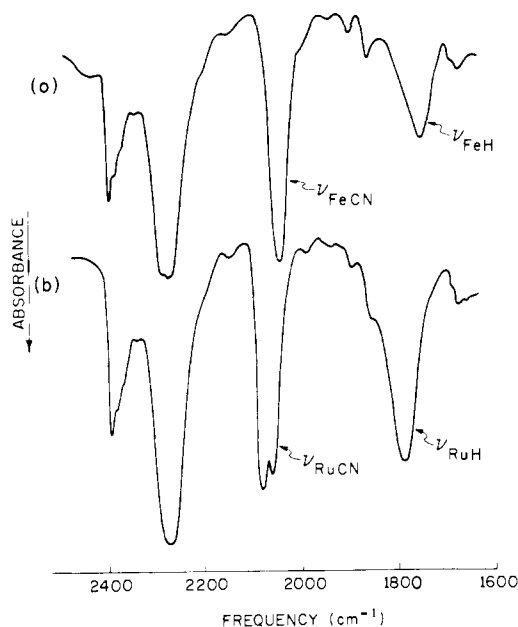
<sup>a</sup> In  $\text{cm}^{-1}$  (in  $\text{C}_6\text{D}_6$ ) with an uncertainty of  $\pm 3 \text{ cm}^{-1}$  for most bands,  $\pm 5 \text{ cm}^{-1}$  for the broader  $\nu_{\text{MH}}$  bands. <sup>b</sup> The decrease in  $\nu_{\text{C}\equiv\text{N}}$  or  $\nu_{\text{C}\equiv\text{C}}$  on forming the *trans* metal hydride complex. <sup>c</sup> The value of  $\nu_{\text{C}\equiv\text{C}}$  is for the gas-phase Raman: G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, Princeton, N.J., 1964, p 290. <sup>d</sup> Mixtures of *cis* and *trans* isomers. The higher frequency  $\nu_{\text{C}\equiv\text{N}}$  band in each case is assigned to the *cis* isomer.

structure is established spectroscopically. The  $^1\text{H}$  NMR spectrum (data in Table 1) shows the hydride as a quintet at high field. The unbroken C-H bond also appears as a quintet, but at lower field and with a much smaller coupling to the four equivalent phosphorus nuclei. The ligand methyl resonances appear as two singlets (each ~6 Hz wide) at  $\delta$  1.56 and 1.16, assigned to  $\text{Me}^a$  and  $\text{Me}^b$ , respectively, in **3**. The exceptionally large downfield shift of  $\text{Me}^a$  [compare  $\delta$  1.35 and 1.21 in *trans*- $\text{HFeNp}(\text{dmpe})_2$ <sup>10</sup>] is a consequence of the proximity of the methyl group to the  $\text{C}\equiv\text{C}$  bond. The  $^{31}\text{P}$   $\{^1\text{H}\}$  NMR spectrum shows a singlet, as expected. The IR spectrum (Table 11) shows bands assignable to stretching vibrations of the  $\text{HFeC}\equiv\text{CH}$  unit. Phenyl- and *tert*-butylacetylides give analogous complexes. Stretching frequencies of 1720 ( $\nu_{\text{FeH}}$ ) and 2036  $\text{cm}^{-1}$  ( $\nu_{\text{C}\equiv\text{C}}$ ) in  $\text{HFeC}\equiv\text{CPh}(\text{dmpe})_2$  can be compared with 1850 and 2035  $\text{cm}^{-1}$  in  $\text{HFeC}\equiv\text{CPh}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2$ .<sup>3d,4c</sup>

While the reaction of terminal acetylenes with **2a** requires a few hours to go to completion at 25 °C, HCN reacts on mixing to give **4a**.<sup>13</sup> No *cis* isomer was detected in the  $^1\text{H}$



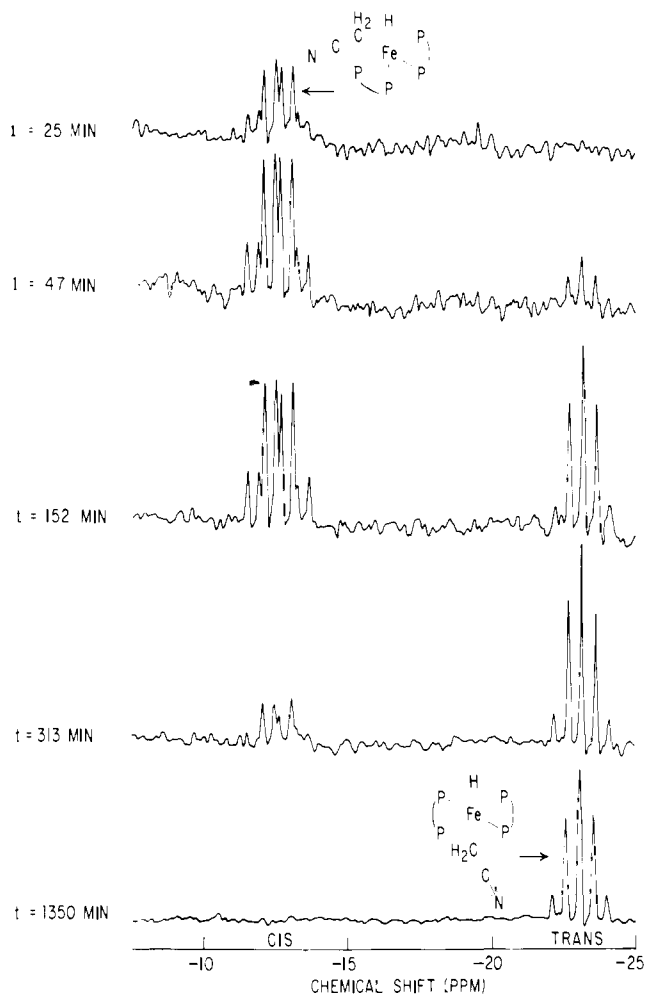
a, M = Fe  
b, M = Ru  
c, M = Os



**Figure 1.** IR spectra of ~0.1 M solutions in  $\text{C}_6\text{D}_6$  in a 0.1-mm cell: (a) *trans*- $\text{HFeCN}(\text{dmpe})_2$ , (b) a mixture of *cis*- and *trans*- $\text{HRuCN}(\text{dmpe})_2$  (70% *cis* by NMR).

NMR spectrum run soon (15 min) after mixing; the spectrum did not change on standing. HCN also reacts rapidly with **2b**, in this case to give an equilibrium mixture of about 85% *cis* and 15% *trans* isomer, as determined by  $^1\text{H}$  NMR. Figure 1 shows IR spectra of  $\text{HFeCN}(\text{dmpe})_2$  and  $\text{HRuCN}(\text{dmpe})_2$ ; the stronger, higher frequency  $\nu_{\text{RuCN}}$  band is tentatively assigned to the major *cis* isomer. The reaction of HCN with **2c** gives ~30% *cis*- and 70% *trans*- $\text{HOsCN}(\text{dmpe})_2$ . The decreasing *trans*:*cis* isomer ratio in the sequence  $\text{Fe} > \text{Os} > \text{Ru}$  is a general feature of  $\text{HMR}(\text{dmpe})_2$  complexes.

**Cleavage of  $\text{sp}^3$  C-H Bonds.** The reaction of acetonitrile with **2a** to give *trans*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$  was cited earlier.<sup>12</sup> Kinetic studies show that the reaction proceeds through *cis*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$  as an intermediate.  $^1\text{H}$  NMR spectra of the hydride region at various times are shown in Figure 2. After 25 min at 25 °C the only hydride resonance easily observed is that of *cis*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$  at  $\delta$  -12.5. The doublet of quartets is a consequence of three nearly equal *cis* P-H couplings and a fourth smaller *trans* coupling. The near absence of  $\text{HFeNp}(\text{dmpe})_2$  resonances in the spectrum after 25 min is due to the fact that most of the Fe is present as  $\text{DFeC}_6\text{D}_5(\text{dmpe})_2$ .<sup>14</sup> At 47 min the *cis* hydride NMR pattern is stronger but a new quintet from *trans*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$

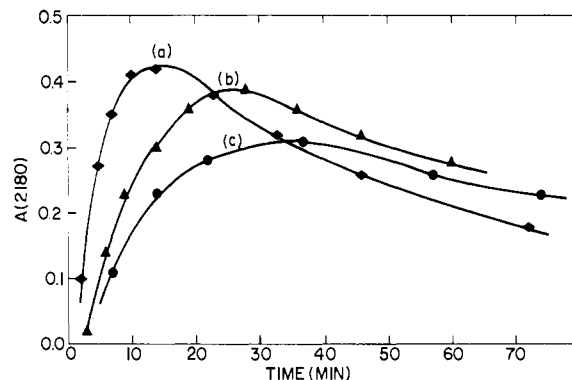


**Figure 2.** 100-MHz  $^1\text{H}$  NMR spectra of the hydride region during the reaction of  $\sim 0.2$  M  $\text{DFe}(\text{C}_6\text{D}_5)(\text{dmpe})_2$  with  $\sim 0.3$  M  $\text{CH}_3\text{CN}$  in  $\text{C}_6\text{D}_6$  at ambient temperature.

is evident at higher field. Eventually the isomerization goes to completion and only the trans isomer is observed. In addition to the hydride quintet, the final spectrum (Table III) shows a quintet at  $-0.6$  ppm with an area twice as large and a much smaller  $J_{\text{PH}} = 5.5$  Hz, assigned to the protons of the  $-\text{CH}_2\text{CN}$  group. In agreement with the trans geometry, the aliphatic region shows two types of dmpe methyl resonances at  $\delta$  1.26 and 1.05.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra, followed with time, show the growth and decay of an ABCD pattern assigned to  $\text{cis-HFeCH}_2\text{CN}(\text{dmpe})_2$ , going finally to the singlet of the trans isomer. The composition of the final product is also established by its elemental analysis (Experimental Section) and high-resolution mass spectrum.<sup>15</sup>

Infrared spectra taken at various times during the reaction of  $\text{HFeNp}(\text{dmpe})_2$  and  $\text{CH}_3\text{CN}$  ( $2250\text{ cm}^{-1}$  in THF) show the gradual loss of their bands and the appearance of a new  $\nu_{\text{CN}}$  band of  $\text{cis-HFeCH}_2\text{CN}(\text{dmpe})_2$  at  $2180\text{ cm}^{-1}$ . This band grows and subsequently decays, as shown in Figure 3, to be replaced by a stronger band from  $\text{trans-HFeCH}_2\text{CN}(\text{dmpe})_2$  at  $2165\text{ cm}^{-1}$ . The infrared spectrum provides a convenient method for detailed kinetic studies of the reaction (see below). The  $\text{C}\equiv\text{N}$  stretching frequencies are unusually low for  $\alpha$ -cyanomethyl complexes. Literature frequencies are  $2183\text{ cm}^{-1}$  in  $\text{trans-HPtCH}_2\text{CN}(\text{PPh}_3)_2$ <sup>16</sup> and  $2206\text{ cm}^{-1}$  in  $\text{CuCH}_2\text{CN}$ .<sup>17</sup> The low frequency suggests that the  $\text{CH}_2\text{CN}$  group in  $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$  has significant carbanion character.<sup>18</sup>

The Ru complex **2b** reacts much more slowly with acetoni-



**Figure 3.** Time dependence of the absorbance at  $2180\text{ cm}^{-1}$  [ $\text{cis-HFeCH}_2\text{CN}(\text{dmpe})_2$ ] in the reaction of  $0.2\text{ M}$   $\text{CH}_3\text{CN}$  with  $0.04\text{ M}$   $\text{HFeNp}(\text{dmpe})_2$  in THF at  $40\text{ }^\circ\text{C}$  ( $0.5\text{-mm}$  cell). Added naphthylene: (a) none, (b)  $0.25\text{ M}$ , (c)  $1.0\text{ M}$ .

trile than **2a**. After 3 days at room temperature a solution of **2b** and  $\text{CH}_3\text{CN}$  in  $\text{C}_6\text{D}_6$  showed only  $\sim 5\%$  reaction. This implies a half-life of reaction of about 40 days. After heating for 22 h at  $60\text{ }^\circ\text{C}$ , the reaction is nearly complete to give  $\text{cis-HRuCH}_2\text{CN}(\text{dmpe})_2$  as the only detectable product. The hydride resonance appears as a doublet of quartets and the  $-\text{CH}_2\text{CN}$  as a stronger doublet of quartets at lower field with smaller P-H couplings (Table III). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows the expected ABCD pattern while the infrared spectrum (Table IV) shows bands assigned to  $\nu_{\text{CN}}$  and  $\nu_{\text{RuH}}$ . Cleavage of the C-H bond in our system is in contrast to the formation of  $(\pi\text{-CH}_3\text{CN})\text{Ru}(\text{PPh}_3)_4\cdot\text{CH}_3\text{CN}$  ( $\nu_{\text{CN}}$  bands at  $1912$  and  $2254\text{ cm}^{-1}$ ) reported for the reduction of  $\text{RuCl}_2(\text{PPh}_3)_4$  in  $\text{CH}_3\text{CN}$ .<sup>19</sup>

The osmium complex **2c** is even less reactive than **2b**. No reaction with excess  $\text{CH}_3\text{CN}$  was detected after heating the  $\text{C}_6\text{D}_6$  solution for 18 h at  $60\text{ }^\circ\text{C}$ , or even on further heating for 60 h at  $75\text{ }^\circ\text{C}$ . The only change in the solution was isomerization of the originally nearly all  $\text{cis-HOsNp}(\text{dmpe})_2$  to  $\sim 25\%$  trans.

Other activated  $\text{CH}_3\text{X}$  compounds ( $\text{X} = -\text{COR}$ ,  $-\text{CO}_2\text{R}$ ,  $-\text{SOR}$ ,  $-\text{SO}_2\text{R}$ ) also react with **2a** and **2b** to form  $\text{HMCH}_2\text{X}(\text{dmpe})_2$  complexes. Table III gives NMR data with the Fe compounds listed first, in order of increasing high-field  $^1\text{H}$  NMR shift of the trans hydride. (This is invariably found at higher field than the cis resonances.) The Ru complexes give hydride resonances at lower field than the corresponding Fe complexes; the same is true for the resonance of  $\text{MCH}_2\text{X}$  protons, which in some cases were obscured by dmpe resonances when  $\text{M} = \text{Ru}$ . The cis hydride resonances of both Fe and Ru complexes (Table III) appear as the X portions of apparent  $\text{AB}_3\text{X}$  spin systems (actually  $\text{ABCDX}$  spin systems). The coupling between the hydride and the trans phosphorus atom is smaller than those observed between the hydride and the cis phosphorus atoms for all iron complexes; the reverse is true for the ruthenium complexes.

In most cases NMR spectra of the iron complexes were run after the solutions had stood overnight at room temperature. Under these conditions product isomerization to the trans iron hydrides was usually so complete that cis hydride resonances were weak or (as in the case of acetonitrile) absent from the spectra. In the methyl acetate and acetone cases the terminal  $\text{CH}_3$  groups, which appeared as singlets well separated from the dmpe resonances, gave a convenient and accurate measure of the isomer distributions, which were 77% trans for  $\text{HFe-CH}_2\text{COOCH}_3(\text{dmpe})_2$  and 85% trans for  $\text{HFe-CH}_2\text{COCH}_3(\text{dmpe})_2$ .  $\text{HRuCH}_2\text{COCH}_3(\text{dmpe})_2$ , by contrast, was only 30% trans, reflecting the greater preference of Ru for cis isomers.  $^1\text{H}$  NMR spectra of  $\text{HRuCH}_2\text{COCH}_3(\text{dmpe})_2$  at temperatures from  $-46$  to  $82\text{ }^\circ\text{C}$  showed only a very small

**Table III.**  $^{31}\text{P}$  and  $^1\text{H}$  NMR Data<sup>a</sup> for  $\text{HMR}(\text{dmpe})_2$  Complexes Where  $\text{R} = \text{CH}_2\text{X}$ ,  $\text{CHXY}$ , or  $\text{SiMe}_3$ 

complex	$^{31}\text{P}$ NMR	$^1\text{H}$ NMR		
		hydride <sup>d</sup>	$-\text{CH}_2\text{X}$ or $-\text{CHXY}$	other
<i>trans</i> - $\text{HFeCH}_2\text{SOCH}_3$	-67.9 s	-21.67 qu (49)	0.84 qu (5)	2.37 s
<i>trans</i> - $\text{HFeCH}_2\text{CN}$	-72.9 s	-23.20 qu (47.5)	-0.59 qu (5.5)	
<i>cis</i> - $\text{HFeCH}_2\text{CN}$	<i>b, c</i>	-12.50 dq (38, 58)		
<i>trans</i> - $\text{HFeCH}_2\text{SO}_2\text{CH}_3$	-71.4 s	-23.31 qu (50.5)	0.98 qu (5.4)	2.65 s
<i>trans</i> - $\text{HFeCH}_2\text{COOCH}_2\text{CH}_3$ ( <b>15a</b> )	-72.3 s	-24.15 qu (51)	0.27 qu (6)	4.04 q (7), 0.95 t (7)
<i>trans</i> - $\text{HFeCH}_2\text{COOCH}_3$ ( <b>15b</b> )	-72.2 s	-24.24 qu (48)	0.24 qu (5.7)	3.48 s
<i>cis</i> - $\text{HFeCH}_2\text{COOCH}_3$	<i>b</i>	-12.22 m		3.60 s
<i>trans</i> - $\text{HFeCH}_2\text{COCH}_3$	-72.9 s	-25.54 qu (50.5)	0.70 qu (5.3)	2.05 s
<i>cis</i> - $\text{HFeCH}_2\text{COCH}_3$	<i>b</i>	-12.30 dq (43, 56)		2.14 s
<i>trans</i> - $\text{HFeCHCN}(\text{COOCH}_3)$ ( <b>5</b> )	-70.7 s	-26.74 qu (48)	3.12 br	4.01 s
<i>trans</i> - $\text{HFeCHCN}(\text{CN})$ ( <b>6</b> )	-70.7 s	<i>e</i>		
<i>cis</i> - $\text{HFeCHCN}(\text{CH}_2\text{CN})$ ( <b>7</b> )	<i>b</i>	-13.69 dq (38, 56)		
<i>trans</i> - $\text{HFeCHCN}(\text{CH}_3)$ ( <b>8</b> )	-72.8 s	-27.50 qu (48)		
<i>cis</i> - $\text{HFeCHCN}(\text{CH}_3)$	<i>b</i>	-13.22 dq (36, 59)		
<i>trans</i> - $\text{HFeCHC}_6\text{H}_5(\text{COCH}_3)$ ( <b>11</b> )	-69.9 s	-32.37 qu (50)	3.17 qu (4)	1.39 s
<i>trans</i> - $\text{HFeCH}_2\text{COCH}_2\text{C}_6\text{H}_5$ ( <b>12</b> )	-72.6 s			
<i>trans</i> - $\text{HFeSiMe}_3$	-74.9 s	-23.4 qu (55)		0.12 s
<i>cis</i> - $\text{HFeSiMe}_3$	<i>b</i>	-14.3 dq (20, 50)		0.62 s
<i>cis</i> - $\text{HRuCH}_2\text{CN}$	<i>b</i>	-8.95 dq (93, 25)	0.37 dq (13.6, 6.0)	
<i>trans</i> - $\text{HRuCH}_2\text{COCH}_3$	-41.6 s	-16.74 qu (22.5)		2.12 s
<i>cis</i> - $\text{HRuCH}_2\text{COCH}_3$	<i>b</i>	-8.89 dq (92.5, 24.5)		2.49 s

<sup>a</sup> In  $\text{C}_6\text{D}_6$ . See Table I for units and abbreviations. For brevity the two dmpe ligands are omitted in the list of complexes. <sup>b</sup> Incompletely resolved ABCD pattern. <sup>c</sup> The *cis* isomer was seen as a transitory intermediate. <sup>d</sup> When there are two numbers in parentheses, the first refers to  $J_{\text{P-H}}$  *trans* and the second to  $J_{\text{P-H}}$  *cis*. <sup>e</sup> The compound is too insoluble in  $\text{C}_6\text{D}_6$  to see the hydride.

**Table IV.** Selected IR Stretching Frequencies<sup>a</sup> in  $\text{HMR}(\text{dmpe})_2$  Complexes Where  $\text{R} = \text{CH}_2\text{X}$  or  $\text{CHXY}$ 

complex	$\nu_{\text{MH}}$	$\nu_{\text{C}\equiv\text{N}}$ or $\nu_{\text{C}=\text{O}}$	$-\Delta\nu^b$	solvent
<i>trans</i> - $\text{HFeCH}_2\text{CN}$	1765	(2181), <sup>c</sup> 2161	90	$\text{C}_6\text{D}_6$
<i>trans</i> - $\text{HFeCH}_2\text{COOCH}_3$	1765	1644	98	$\text{C}_6\text{D}_6$
$\text{HFeCH}_2\text{COCH}_3^d$	1770	1604, 1585, 1576 <sup>d</sup>		THF
<i>trans</i> - $\text{HFeCHCN}(\text{COOCH}_3)$ ( <b>5</b> )	1795	2170, 1620	90, 135	$\text{C}_6\text{D}_6$
<i>trans</i> - $\text{HFeCHCN}(\text{CN})$ ( <b>6</b> )	1805	2133	139	THF
<i>cis</i> - $\text{HFeCHCN}(\text{CH}_2\text{CN})$ ( <b>7</b> )	1735 <sup>e</sup>	2178, 2230	73, 21	THF
$\text{HFeCHCN}(\text{CH}_3)$ ( <b>8</b> ) <sup>f</sup>	1770	2163	82	$\text{C}_6\text{D}_6$
<i>cis</i> - $\text{HRuCH}_2\text{CN}(\text{dmpe})_2$	1760 <sup>g</sup>	2171	80	$\text{C}_6\text{D}_6$
$\text{HRuCH}_2\text{COCH}_3(\text{dmpe})_2^f$	1795	1585	126	$\text{C}_6\text{D}_6$

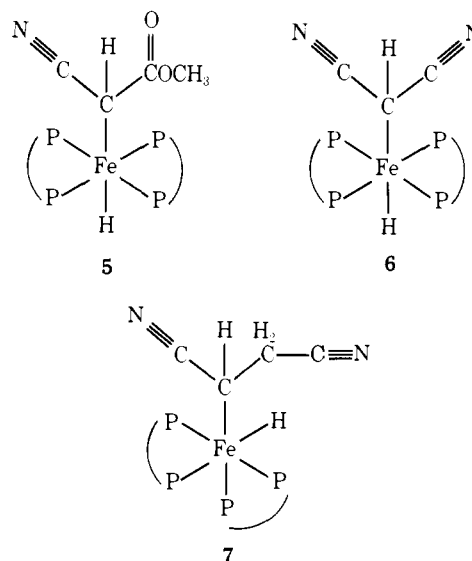
<sup>a</sup> In  $\text{cm}^{-1}$  with an uncertainty in most cases of  $\pm 3$ . The broad  $\nu_{\text{MH}}$  bands are more uncertain and are reported to the nearest  $5 \text{ cm}^{-1}$ . For brevity the two dmpe ligands are omitted in the list of complexes. <sup>b</sup> The decreases in  $\nu_{\text{C}\equiv\text{N}}$  or  $\nu_{\text{C}=\text{O}}$  on forming the metal hydride complex. Values of  $\nu_{\text{C}\equiv\text{N}}$  for the free nitriles were measured in THF, because  $\text{C}_6\text{D}_6$  absorbs strongly in the  $2250\text{-cm}^{-1}$  region. <sup>c</sup> For the transient *cis* isomer in THF. <sup>d</sup> This is a mixture of *cis*- and *trans*- $\text{HFeCH}_2\text{COCH}_3(\text{dmpe})_2$  and  $(\text{dmpe})_2\text{HFeCH}_2\text{COCH}_2\text{FeH}(\text{dmpe})_2$ . <sup>e</sup> Freshly prepared  $\text{C}_6\text{D}_6$  solution. <sup>f</sup> A mixture of *cis* and *trans* isomers is indicated by NMR. <sup>g</sup> In Nujol.

temperature dependence<sup>20</sup> in the isomerization equilibrium, consistent with a very small  $\Delta H$  between the two isomers.

As expected, the doubly activated compounds (of general type  $\text{XCH}_2\text{Y}$ ) methyl cyanoacetate, malononitrile, and succinonitrile also give  $\text{HFeR}(\text{dmpe})_2$  adducts (**5**–**7**). Although **6** is too insoluble in  $\text{C}_6\text{D}_6$  for the hydride resonances to be seen easily in the  $^1\text{H}$  NMR spectrum, the  $^{31}\text{P}$  NMR singlet at  $-70.7$  ppm (the same shift as **5**) and strong IR band at  $2133 \text{ cm}^{-1}$  leave little doubt as to its structure. **5** and **7** show bands at slightly higher frequency (Table IV), as assigned to  $\nu_{\text{CN}}$  of the  $\alpha$ -CN group. The  $\beta$ -CN group in **7** cannot be observed in  $\text{C}_6\text{D}_6$  because of strong solvent absorption between  $2200$  and  $2300 \text{ cm}^{-1}$  (seen in Figure 1). Surprisingly, **7** is exclusively the *cis* isomer.

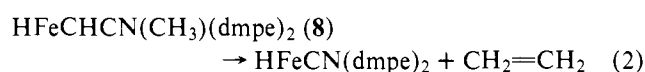
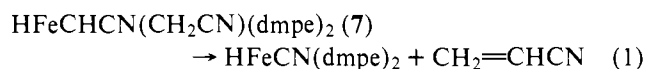
Propionitrile gives a mixture of products, one *cis* and one *trans*, as shown by  $^{31}\text{P}\{^1\text{H}\}$  and the hydride region  $^1\text{H}$  NMR spectra. Unfortunately, the aliphatic region in the  $^1\text{H}$  NMR is too complex, even at  $220 \text{ MHz}$ , to be readily assigned. The branched structure  $\text{HFeCHCN}(\text{CH}_3)(\text{dmpe})_2$  (**8**) seems more likely than the linear  $\text{HFeCH}_2\text{CH}_2\text{CN}(\text{dmpe})_2$  since the  $\nu_{\text{CN}}$  band at  $2165 \text{ cm}^{-1}$  is very similar to that of *trans*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$ ; a higher frequency would be expected if the Fe were bonded to a  $\beta$  carbon.  $\nu_{\text{CN}}$  in *trans*-

$\text{HPt}(\text{CH}_2)_n\text{CN}(\text{PPh}_3)_2$  is  $2083$  for  $n = 1$  and  $2245 \text{ cm}^{-1}$  for  $n = 3$ .<sup>16</sup>

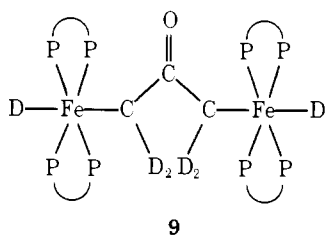


Infrared spectra of solutions of **7** and **8** also showed unexpected bands at about  $2050\text{ cm}^{-1}$ . To investigate bands in the  $2250\text{-cm}^{-1}$  region, the  $\text{C}_6\text{D}_6$  solvent was stripped off (about 1 week after the initial spectra were run) and the residues were redissolved in THF. The solution containing **7** showed bands for the two types of cyano groups at  $2178$  and  $2230\text{ cm}^{-1}$ . The band at  $2055\text{ cm}^{-1}$  was stronger than before. The solution which had contained **8** showed only a strong  $2055\text{-cm}^{-1}$  band, and no remaining bands of **8**. The new band has the same frequency as *trans*- $\text{HFeCN}(\text{dmpe})_2$  in THF; the assignment was confirmed by  $^1\text{H}$  NMR.

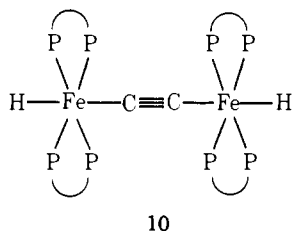
The appearance of  $\text{HFeCN}(\text{dmpe})_2$  is consistent with eq 1 and 2, although we did not identify the olefins formed. These unusual reactions appear to require  $\beta$  hydrogens, as they did not occur with **5** and **6**. Apparently the Fe-C bond in  $\text{HFeCN}(\text{dmpe})_2$ , with an sp-hybridized carbon, is strong enough to drive reactions 1 and 2.



In some cases cleavage of two C-H bonds in the same molecule can lead to dinuclear iron hydrides. Thus a  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum run 5 h after mixing a solution of  $\text{CD}_3\text{COCD}_3$  and **2a** in a 0.5:1 ratio showed 1:1:1 triplets<sup>21</sup> at  $-72.0$  and  $-70.1$  ppm (each with  $J_{\text{PD}} \sim 7$  Hz) assigned to *trans*- $\text{DFeCD}_2\text{COCD}_3(\text{dmpe})_2$  and **9**. No **9** was observed in another experiment with acetone in excess.



Surprisingly, no **10** was detected when acetylene and **2a** were allowed to react in a 0.5:1 ratio. Space-filling models show that

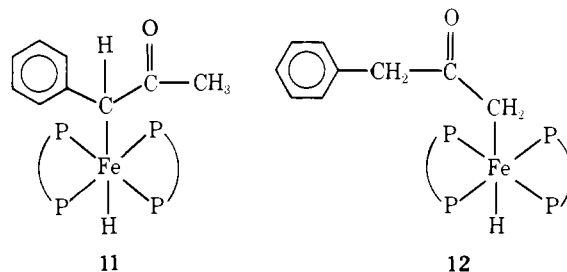


$-\text{C}\equiv\text{C}-$  does not provide a long enough bridge to relieve crowding of the ligands on the two metal centers.

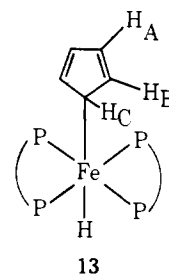
Methyl ethyl ketone reacts with **2a** to give a complex mixture of products with at least six different hydride resonances ranging from  $-8.5$  to  $-33.6$  ppm. Two of the resonances were identified as belonging to unreacted *cis*- and *trans*- $\text{HFeNp}(\text{dmpe})_2$ . The presence of unreacted starting complex, after days in the presence of 50% excess ketone, shows that methyl ethyl ketone gives less stable products than acetone.

Phenylacetone gives a mixture of **11** and **12** in a 20:1 ratio. The  $^{31}\text{P}$  NMR chemical shift of **12** is close to that of *trans*- $\text{HFeCH}_2\text{COCH}_3(\text{dmpe})_2$  (Table II). The hydride resonance of **11** is at exceptionally high field, apparently a general feature for  $\text{HFeR}(\text{dmpe})_2$  complexes where R is attached by a secondary carbon. Structure **11** is supported by the  $\nu_{\text{CO}}$  band at  $1591\text{ cm}^{-1}$ . The predominance of this isomer can be rationalized in terms of resonance stabilization of the carbanion fragment.

Formation of  $\text{HFeR}(\text{dmpe})_2$  complexes by cleavage of sp<sup>3</sup>

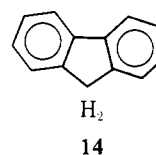


C-H bonds does not require that R contain strongly electron-withdrawing groups like carbonyl or nitrile, but does require that R<sup>-</sup> be a relatively stable carbanion.<sup>22</sup> Cyclopentadiene gives **13**,<sup>23</sup> identified as a monohapto cyclopentadiene



complex by the ring proton NMR resonances in a 2:2:1 intensity ratio at  $\delta$  6.50 d (8), 6.30 d (8), and 4.00 br at ambient temperature. The hydride appears as a quintet at  $\delta -30.2$  ( $J_{\text{PH}} = 49.5$  Hz) in the  $^1\text{H}$  NMR spectrum and as a band at  $1788\text{ cm}^{-1}$  in the IR. A *trans* geometry is supported by the  $^{31}\text{P}$  NMR singlet at  $-69.9$  ppm. The cyclopentadienyl chemical shifts are close to those reported ( $\delta$  6.3, 6.0, and 3.5) for the fluxional  $\eta_1$  ring of  $\text{Fe}(\text{C}_2)(\eta_5\text{-C}_5\text{H}_5)[\eta_1\text{-C}_5\text{H}_5]$ <sup>24</sup> in the slow exchange limit. The complex **13** is one of the rare examples of a nonfluxional  $\eta_1$ -cyclopentadienyl complex. The tightly bound dmpe ligands lock **13** into an 18-electron configuration, with no readily available 16-electron pathway for exchange.

The reaction of **2a** with fluorene (**14**) in slight excess did not produce a cyclopentadienyl-type adduct. A large excess of **14**

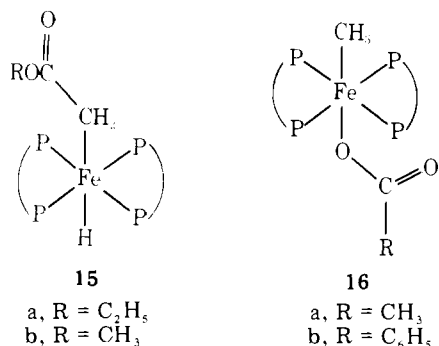


gave aryl C-H cleavage (identified by characteristic NMR shifts)<sup>11</sup> rather than reaction at the methylene. This result is attributed to unfavorable steric interactions with the two benzo groups. Similar results were obtained with triphenylmethane and indene.

We have not observed reactions of **2a** with  $\text{CH}_3\text{CF}_3$ , pentane, or cyclopropane. Reaction with trimethylsilane did, however, give a mixture of about 60% *cis*- and 40% *trans*- $\text{HFeSiMe}_3(\text{dmpe})_2$ . The trimethylsilyl adduct represents the only case in which the substrate had no means of coordination to the metal prior to oxidative addition. Unfortunately, we were not able to confirm addition through a *cis* intermediate because both *cis* and *trans* isomers were observed even in the initial stages of reaction.

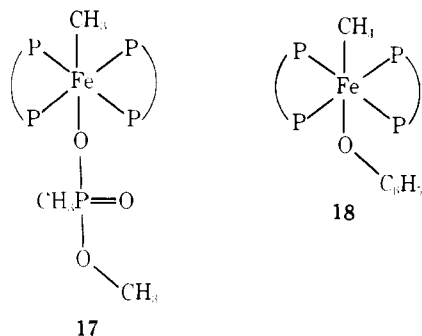
**Cleavage of C-O Bonds.** Ethyl acetate reacts only at a C-H bond adjacent to the ester carbonyl to give **15a**. The  $\text{Fe-CH}_2\text{CO}_2^-$  group gives a quintet in the  $^1\text{H}$  NMR at about 0.3 ppm downfield of  $\text{Me}_4\text{Si}$ , with  $J_{\text{PH}} = 6$  Hz, in addition to the hydride resonance at  $-24.2$  ppm ( $J_{\text{PH}} \sim 50$  Hz).

Methyl acetate gives **15b** with NMR parameters (Table III) very similar to those of **15a**; however, it also gives  $\sim 25\%$  of **16a**, identified by a quintet at 3.3 ppm upfield of  $\text{Me}_4\text{Si}$  in the  $^1\text{H}$  NMR spectrum with  $J_{\text{PH}} = 7$  Hz, and in the  $^{31}\text{P}\{^1\text{H}\}$  NMR



spectrum a singlet at  $-70$  ppm. Similar NMR parameters (Table 11) are obtained in the reaction of methyl benzoate to give **16b**, which has IR bands assigned to coordinated benzoate at  $1565$  and  $1346$   $\text{cm}^{-1}$ . About 70% of the product is **16b**, the rest being isomers resulting from aromatic C-H bond cleavage.<sup>11</sup> Ethyl benzoate gives no detectable C-O bond cleavage. One possible explanation of the difference in behavior of methyl acetate or benzoate as opposed to the ethyl esters is steric, since the methyl group has a smaller cone angle ( $90^\circ$ ) than the ethyl group ( $102^\circ$ ).<sup>25</sup>

Methyl dimethylphosphonite,  $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ , reacts exclusively by cleavage of a C-O bond, giving **17**. The  $^1\text{H}$



NMR spectrum shows three types of substrate methyl, the one on iron appearing as a quintet ( $J_{\text{PH}} = 7.0$  Hz) at  $-3.61$  ppm. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum shows two types of phosphorus in a 4:1 intensity ratio at  $-68.4$  and  $-16.2$  ppm assigned to the dmpe and phosphonite resonances, respectively; no P-P coupling was resolved. At equilibrium anisole gives exclusively **18**, with a  $^{31}\text{P}\{^1\text{H}\}$  NMR singlet at  $-68.4$  ppm. Cleavage of the methyl-oxygen bond of anisole, but not of THF, is probably a consequence of the stability of the phenoxide ion. Work on other substituted benzenes<sup>11</sup> indicates that a methoxy group deactivates the aromatic C-H bonds.

The  $\text{CH}_2\text{NO}_2^-$  anion is also very stable; however, treatment of **2a** with  $\text{CH}_3\text{NO}_2$  caused immediate destruction of the complex. The only  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances detected were those of oxidized dmpe. By contrast  $\text{Ir}(\text{dmpe})_2^+$  is more resistant to destructive oxidation and  $[\text{HlrCH}_2\text{NO}_2(\text{dmpe})_2]^+$  can be isolated.<sup>7</sup>

**Cleavage of C-Halogen Bonds.** Methyl iodide reacts with **2a** to give  $\text{CH}_3\text{FeI}(\text{dmpe})_2$  rather than the isomeric  $\text{HFeCH}_2\text{I}(\text{dmpe})_2$ . NMR data are given in Table V.

$\text{NCCH}_2\text{Cl}$  (50% excess) reacts with **2a** to give a mixture of trans products with the following  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts and approximate percentages:  $-68.1$  (50%),  $-64.0$  (10%), and  $-58.3$  ppm (40%). The last is clearly assigned to *trans*- $\text{FeCl}_2(\text{dmpe})_2$ , on the basis of  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shift and the  $^1\text{H}$  NMR spectrum. The proton spectrum also showed a sharp resonance at  $\delta$  0.60 assigned to  $\text{CH}_3\text{CN}$ . No resonances were observed at higher field; however, a weak IR band at  $2176$   $\text{cm}^{-1}$  suggests the presence of some  $\text{FeCH}_2\text{CN}$ .

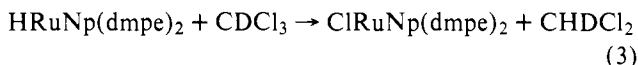
Excess chlorobenzene, allyl chloride,  $\text{CDCl}_3$ , and  $\text{HCl}$  also gave *trans*- $\text{FeCl}_2(\text{dmpe})_2$  as the major product.<sup>26</sup> The latter

Table V.  $^{31}\text{P}$  and  $^1\text{H}$  NMR Data<sup>a</sup> for  $\text{CH}_3\text{FeX}(\text{dmpe})_2$  Complexes

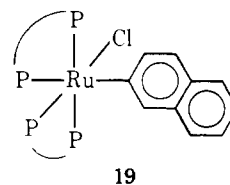
complex	$^{31}\text{P}$ NMR	$^1\text{H}$ NMR	
		$\text{CH}_3\text{Fe}$	other
$\text{CH}_3\text{FeOCOCH}_3$ ( <b>16a</b> )	$-70.2$ s	$-3.29$ qu (7.3)	$3.60$ s
$\text{CH}_3\text{FeOCOC}_6\text{H}_5$ ( <b>16b</b> )	$-70.0$ s	$-3.18$ qu (7.0)	
$\text{CH}_3\text{FeOP}(\text{O})\text{CH}_3$ ( $\text{OCH}_3$ ) ( <b>17</b> )	$-68.4$ s	$-3.61$ qu (7.0)	$3.48$ d (10), $0.96$ d (17)
$\text{CH}_3\text{FeOC}_6\text{H}_5$ ( <b>18</b> )	$-68.4$ s	$-3.47$ qu (7.0)	
$\text{CH}_3\text{FeI}$	$-64.1$ s	$-2.60$ qu (7.3)	

<sup>a</sup> In  $\text{C}_6\text{D}_6$ . Shift conventions and abbreviations as in Table I.

two reactions appeared to occur immediately upon mixing. The reaction of  $\text{CDCl}_3$  with **2b** (50% excess  $\text{CDCl}_3$ , heated overnight at  $60$   $^\circ\text{C}$ ) gave about 20% *trans*- $\text{RuCl}_2(\text{dmpe})_2$ ,<sup>10</sup> but the major product was **19**, identified by its ABCD  $^{31}\text{P}\{^1\text{H}\}$  NMR pattern ( $-48.6$ ,  $-37.4$ ,  $-36.2$ , and  $-19.1$  ppm) and assignment of the aromatic hydrogens in the proton spectrum.<sup>27</sup> Thus the major reaction is given by

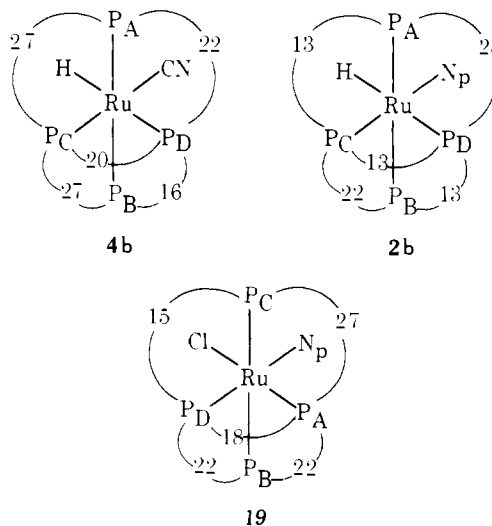


The  $\text{CHDCl}_2$  produced was clearly identified by its 1:1:1 triplet pattern ( $J_{\text{HD}} = 0.7$  Hz) in  $^1\text{H}$  NMR. Structure **19** below can



be confidently drawn with  $\text{P}_A$  trans to  $\text{Cl}$  on the basis that its chemical shift ( $-48.6$  ppm) is well downfield of those of  $\text{P}_B$  and  $\text{P}_C$  ( $-37.4$  and  $-36.2$  ppm), which are close together and therefore represent phosphines trans to each other. An ordering of  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts based on the trans ligand in the sequence  $\text{H} < \text{P} < \text{Cl}$  was observed earlier in  $\text{Rh}(\text{I})$  complexes.<sup>28</sup>

The cis P-P coupling constants (Hz) in **4b**, **2b**,<sup>10</sup> and **19** show an interesting trans effect. The  $^{31}\text{P}$  nuclei are given subscript designations showing their order from low to high field. Couplings to  $\text{P}_C$  in **4b** are uniformly larger than in **2b** by



$5$ – $14$  Hz, but the other  $^2J_{\text{PP}}$  are the same to within 3 Hz. Couplings to  $\text{P}_A$  in **19** are uniformly larger than those to  $\text{P}_D$  in **2b** by 2–9 Hz, but the other  $^2J_{\text{PP}}$  are the same to within 2 Hz.

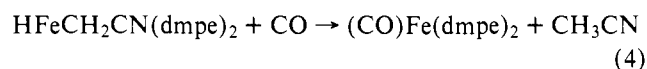
**Table VI.** Kinetics of Reaction of CH<sub>3</sub>CN with HFeNp(dmpe)<sub>2</sub> in THF

temp. °C	[CH <sub>3</sub> CN], M	[HNp] added, M	10 <sup>2</sup> k <sub>3</sub> , <sup>a</sup> min <sup>-1</sup>	t <sub>m</sub> , <sup>b</sup> min	10 <sup>2</sup> k, <sup>c</sup> min <sup>-1</sup>
25	0.4	0.0	(0.16) <sup>d</sup>	110	2.8
	1.2	0.0	0.14	130	2.3
	3.8	0.0	(0.16) <sup>d</sup>	130	2.2
	3.9	0.0	0.17	150	1.7
	0.16	0.16	0.17	210	1.0
	mean			0.16 ± 0.2	
40	0.2	0.0	3.4	15	12
	0.33	0.0	3.1	16	11
	0.5	0.0	3.0	14	14
	4.7	0.0	1.5	20	12
	0.2	0.25	2.4	22	7.6
	0.33	0.25	2.6	19	9.2
	4.7	0.25	1.9	20	10.3
	0.2	0.5	2.1	28	5.8
	0.33	0.5	2.5	23	7.0
	1.0	0.5	2.6	20	8.5
	0.2	1.0	1.9	35	4.0
	0.33	1.0	2.1	30	5.0
	1.0	1.0	2.0	24	7.5
	4.7	1.0	1.2	26	8.8
	mean			2.3 ± 0.5	

<sup>a</sup> Determined from the slope of a plot of  $\ln [A_{\infty}(2165) - A(2165)]$  against  $t$ . <sup>b</sup> Time to the maximum value of  $A(2180)$ . <sup>c</sup> Pseudo-first-order rate constant for the appearance of  $A(2180)$ . Obtained by successive approximations of eq 8. <sup>d</sup> Not actually determined, but taken to be the mean of the others. <sup>e</sup> Mean for runs without added naphthylene.

It appears that the values of  $cis\text{-}^2J_{PP}$  depend on the electro-negativity of the ligands trans to the phosphorus nuclei in question, decreasing in the order  $CN > Cl > H \approx Np$ .

**Reactions of HFeCH<sub>2</sub>CN(dmpe)<sub>2</sub> with CO and CO<sub>2</sub>.** Reactions were carried out to see if CO or CO<sub>2</sub> could be inserted into the metal-carbon bond of the acetonitrile adduct. Reaction of preformed HFeCH<sub>2</sub>CN(dmpe)<sub>2</sub> with CO overnight at room temperature gave a partial reaction according to

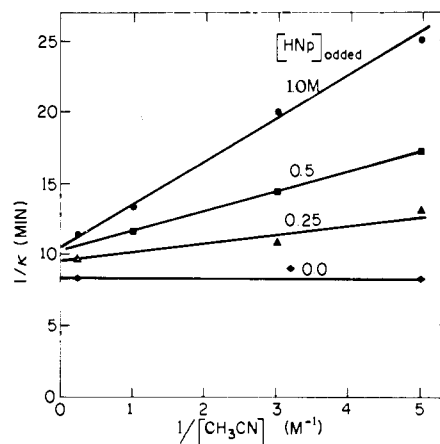


No aldehyde or HFeCOCH<sub>2</sub>CN(dmpe)<sub>2</sub> was detected. Even heating for 18 h at 60 °C under 15 psig CO did not give complete reaction. This shows that reductive elimination of acetonitrile is much slower than elimination of naphthylene from **2a**.

In another experiment **2a** partially dissolved in neat CH<sub>3</sub>CN after stirring for 4 h to give an IR band at 2176 cm<sup>-1</sup> assigned to HFeCH<sub>2</sub>CN(dmpe)<sub>2</sub>. Within 5 min of adding CO<sub>2</sub>, all the solids dissolved to give a yellow solution of a cyanoacetate complex with strong, broad, new bands at 1585 and 935 cm<sup>-1</sup>. After stirring overnight, little if any of the 2176-cm<sup>-1</sup> band remained. Heating overnight at 60 °C gave a new, strong band of free cyanoacetic acid at 1730 cm<sup>-1</sup>. Treatment with Br<sub>2</sub> or I<sub>2</sub> gave free cyanoacetic acid and a product without the bands at 1585 and 935 cm<sup>-1</sup>. Further treatment with CH<sub>3</sub>OH/BF<sub>3</sub> gave NCCH<sub>2</sub>COOMe, detected by gas chromatography/mass spectroscopy.

Coupling of acetonitrile and CO<sub>2</sub> by a transition metal complex is a novel reaction without much precedent. It has been achieved with some closely related electron-rich complexes of Ir(I).<sup>7</sup> Some metal hydrides react with CO<sub>2</sub> to give metal formates.<sup>29</sup>

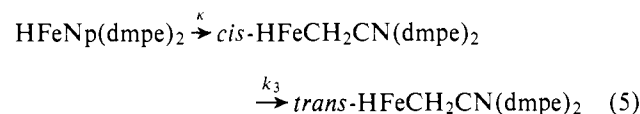
**Kinetics of the Reaction of CH<sub>3</sub>CN with HFeNp(dmpe)<sub>2</sub>.** Kinetic studies were carried out to suggest possible mechanisms for this reaction. The sharp IR bands of  $\nu_{CN}$  in *cis*- and *trans*-HFeCH<sub>2</sub>CN(dmpe)<sub>2</sub> were used to follow the reaction



**Figure 4.** Plot of  $1/k$  against  $1/[CH_3CN]$  for the reaction of CH<sub>3</sub>CN with HFeNp(dmpe)<sub>2</sub> in THF at 40 °C, with various concentrations of added naphthylene. The error bars show an uncertainty of ±10%.

of CH<sub>3</sub>CN with **2a** in THF. This solvent was chosen because it does not react with **2a** and is transparent in the IR in the region of interest. Figure 3 shows that added naphthylene inhibits the formation of *cis*-HFeCH<sub>2</sub>CN(dmpe)<sub>2</sub>, but not the rate of its isomerization to the *trans* isomer. The extent of the inhibition, however, depends on the concentration of acetonitrile. This can be seen in the data obtained at 40 °C in Table VI. Most of the runs were carried out at this temperature to obtain conveniently measurable rates.

On the basis of the 16- and 18-electron rule,<sup>30</sup> we anticipated that the reaction would proceed as shown in Scheme 1.<sup>31</sup> Applying the steady-state approximation to the reactive intermediate  $[Fe(dmpe)_2]$  gives the kinetic equivalent of two consecutive first-order reactions:

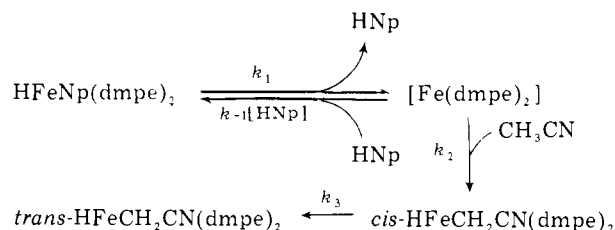


where

$$1/k = 1/k_1 + k_{-1}[HNp]/k_1k_2 \cdot 1/[CH_3CN] \quad (6)$$

A plot of  $1/k$  against  $1/[CH_3CN]$  should give a series of lines which intersect the  $y$  axis at a common point ( $1/k_1$ ), and whose slopes ( $s$ ) are proportional to  $[HNp]$ . That this rate law is indeed followed, within the experimental accuracy, is shown by Figures 4 and 5. The value of  $k_1$ , the rate constant for reductive elimination of naphthylene, is about 0.10 min<sup>-1</sup> at 40 °C. Note that in the absence of added naphthylene the rate of formation of *cis*-HFeCH<sub>2</sub>CN(dmpe)<sub>2</sub> is essentially independent of  $[CH_3CN]$ , and  $k_1$  is rate determining. The value of  $k_1$  determined from the CH<sub>3</sub>CN reaction rate at 25 °C is  $0.022 \pm 0.003$  min<sup>-1</sup> (Table VI). This is equal (within experimental error) to the value of  $0.020 \pm 0.004$  min<sup>-1</sup> determined earlier<sup>10</sup> from rates of CO reaction at 25 °C, consistent with rate-determining loss of HNp in both cases. The temperature dependence of  $k_1$ , while not accurately determined, gives  $\Delta H_1^\ddagger \sim 22$  kcal/mol and  $\Delta S_1^\ddagger \sim 0$ .

Scheme 1



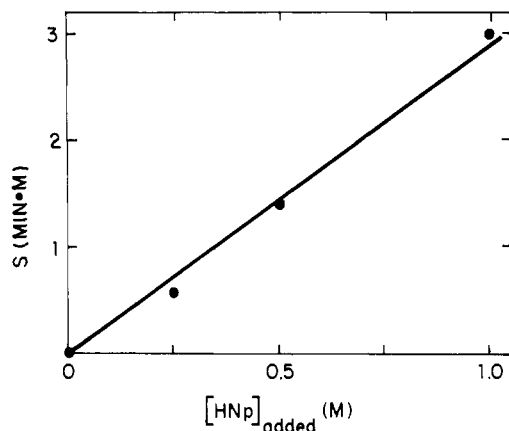
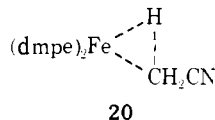


Figure 5. Plot of the slopes of lines in Figure 4 against the concentration of added naphthylene.

From the slope ( $k_1/k_1k_2$ ) of Figure 5 and the value of  $k_1$ , we find that  $k_2/k_1 \sim 3$  at 40 °C, i.e.,  $[\text{Fe}(\text{dmpe})_2]$  reacts with  $\text{CH}_3\text{CN}$  in preference to naphthylene by a factor of about 3.

The data in Table VI show that  $k_3$ , the isomerization rate constant, is essentially independent of  $[\text{CH}_3\text{CN}]$  and  $[\text{HNp}]$ , as expected. The temperature dependence of  $k_3$  gives  $\Delta H_3^\ddagger \sim 32$  kcal/mol and  $\Delta S_3^\ddagger \sim 28$  eu.

**Mechanism of Oxidative Additions.** The fact that *cis*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$  is the kinetically preferred product, even though it is the thermodynamically less stable isomer, is consistent with a three-center transition state **20** for the oxidative



addition step. An analogous structure can be drawn for the oxidative addition of  $\text{H}_2$ .<sup>10</sup> While we find this esthetically pleasing, we cannot rule out pathways involving prior coordination of the  $-\text{CN}$  group (though we saw no spectroscopic evidence for such intermediates). Oxidative addition (C-C cleavage) of cyanogen to  $\text{Pt}(\text{PPh}_3)_4$  gives *cis*- $\text{Pt}(\text{PPh}_3)_2(\text{CN})_2$  initially, which then isomerizes to *trans*- $\text{Pt}(\text{PPh}_3)_2(\text{CN})_2$ .<sup>32</sup> Corain<sup>33</sup> favors coordination of cyanogen as a Lewis base prior to oxidative addition. N-Bonded cyanogen complexes have been observed in some analogous reactions of  $\text{NiL}_4$  complexes.<sup>34</sup>

The failure of 1,1,1-trifluoroethane to react with **2a** supports the position that prior coordination of a substrate is necessary; however, we do not know that  $\text{HFeCH}_2\text{CF}_3(\text{dmpe})_2$  would be more thermodynamically stable than  $\text{HFeNp}(\text{dmpe})_2$ . Oxidative addition of trimethylsilane could not involve prior coordination, but this reaction might involve a free radical chain mechanism.

Most of the oxidative addition and Lewis base adduct forming reactions of **2a** proceed at about the same rate and therefore probably involve reductive elimination of naphthylene as a first step in each case. In contrast, the reactions of  $\text{HCN}$ ,  $\text{HCl}$ ,  $\text{I}_2$ , and  $\text{TCNE}$  occur essentially instantaneously, and the naphthylene must remain coordinated in the first step. The rate differences are even more striking with **2b**, where the half-life for naphthylene loss is  $\sim 40$  days. Electrophilic attack prior to loss of naphthylene is consistent with the observation<sup>8</sup> that reaction of **2b** with  $\text{DCl}$  gives naphthylene labeled by deuterium on C-2, the carbon from which the metal is cleaved.

### Experimental Section

All manipulations were carried out in a dry nitrogen atmosphere. All solvents were dried by standard techniques. Melting points were

measured under nitrogen and are uncorrected. The preparation of  $\text{Fe}(\text{dmpe})_2\text{H}(\text{C}_{10}\text{H}_7)$  has been described previously<sup>10</sup> and all other reactants were commercially available. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker HFX-90 spectrometer at 36.43 MHz. Proton spectra were recorded on Varian HR-220 and XL-100 spectrometers. Analyses were carried out in our analytical facilities.

**Preparation of *trans*- $\text{HFe}(\text{CH}_2\text{CN})(\text{dmpe})_2$ .** A solution of  $\text{HFeNp}(\text{dmpe})_2$  (0.48 g, 1.0 mmol) in tetrahydrofuran (20 mL) was treated with an excess of acetonitrile (0.52 mL, 0.41 g, 10 mmol). The mixture was stirred overnight and the color lightened from gold to yellow. The solution was filtered to remove suspended solids and the solvent was removed under vacuum. The solids were suspended in pentane/ether, collected by vacuum filtration, and dried under vacuum, yield 60%, mp 183 °C.

Anal. Calcd for  $\text{FeP}_4\text{C}_{14}\text{H}_{35}\text{N}$ : C, 42.3; H, 8.88. Found: C, 42.2; H, 8.93.

**Preparation of *trans*- $\text{HFe}(\text{C}_2\text{Ph})(\text{dmpe})_2$ .** The reaction was carried out in a manner analogous to the previous reaction, using phenylacetylene (0.220 mL, 0.20 g, 2 mmol), yield 60%, mp 235 °C.

Anal. Calcd for  $\text{FeP}_4\text{C}_{20}\text{H}_{38}$ : C, 52.4; H, 8.36. Found: C, 52.1; H, 8.50.

Spectroscopic data are given in Tables I and II.

**Microscale Reactions.** Typically 0.1 mmol of  $\text{HMNp}(\text{dmpe})_2$  in a small test tube was treated with 0.15 mmol of reactant in 0.8 mL of  $\text{C}_6\text{D}_6$ . Reactions with gases were carried out by adding the gas by hypodermic syringe to a serum capped tube containing the metal complex in  $\text{C}_6\text{D}_6$ .

When reactions of iron complexes were allowed to proceed overnight at room temperature, the mixtures were usually filtered to remove solid precipitates before running  $^1\text{H}$  NMR spectra. For  $^{31}\text{P}$  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. One of the more involved microscale reactions is detailed below.

**Reaction of  $\text{HFe}(\text{CH}_2\text{CN})(\text{dmpe})_2$  with  $\text{CO}_2$ .** Solid **2a** was dissolved in neat  $\text{CH}_3\text{CN}$  at room temperature to perform the *trans* acetonitrile adduct. After 4 h, the resultant suspension was placed under an atmosphere of  $\text{CO}_2$ . There was a relatively rapid reaction to give a yellow solution of the cyanoacetate complex having new infrared bands at 1585 and 935  $\text{cm}^{-1}$ . The CN stretching vibration expected around 2250  $\text{cm}^{-1}$  was masked by the solvent. After 24 h, the reaction was essentially quantitative as measured by NMR. Free cyanoacetic acid ( $\nu_{\text{C}=\text{O}}$  1730  $\text{cm}^{-1}$ ) was liberated by thermolysis (60 °C for 24 h) or halogenolysis of the yellow solution. The only observed phosphorus-containing product after treatment with  $\text{Br}_2$  was  $\text{Fe}(\text{dmpe})_2\text{Br}_2$ . The yield of cyanoacetic acid was judged to be high as indicated by the infrared spectra. The suspension was filtered and treated with  $\text{CH}_3\text{OH}/\text{BF}_3$  to give methyl cyanoacetate which was detected by GC/MS. No attempt was made to assess the yield of the esterification.

**Kinetics of Reaction of  $\text{CH}_3\text{CN}$  with  $\text{HFeNp}(\text{dmpe})_2$ .** Reactions were carried out in a 0.5-mm IR cell in a Barnes Engineering Model 104 variable temperature chamber, whose temperature was monitored by a thermocouple. Solutions containing 0.04 M  $\text{HFeNp}$  and variable concentrations of  $\text{CH}_3\text{CN}$  and added naphthylene in deoxygenated THF were prepared under  $\text{N}_2$  and quickly transferred by syringe to the  $\text{N}_2$ -flushed, preheated IR cell. Spectra were repetitively swept over the range 2400–1900  $\text{cm}^{-1}$ , and absorbances determined at 2180 [*cis*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$ ] and 2165  $\text{cm}^{-1}$  [*trans*- $\text{HFeCH}_2\text{CN}(\text{dmpe})_2$ ] as a function of time. Typical plots of  $A(2180)$  against time are shown in Figure 3.  $A(2165)$  increases monotonically in such a way that plots of  $\ln [A_\infty(2165) - A(2165)]$  against time are linear over 3 half-lives, once  $A(2180)$  has passed through its maximum.

Rate data at 25 and 40 °C are given in Table VI. Values of  $\kappa$  were determined from  $t_m$ , the time required for  $A(2180)$  to pass through a maximum value, by solving the transcendental equation

$$\exp[-\kappa t_m] = k_3/\kappa \exp[-k_1 t_m] \quad (7)$$

by successive approximation. This was most conveniently done by rearranging as in

$$\kappa_{n+1} = k_3 \exp[(\kappa_n - k_1)t_m] \quad (8)$$

where  $\kappa_n$  is the  $n$ th approximation to  $\kappa$  and  $\kappa_{n+1}$  is the  $(n+1)$ th.



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- (13) The mass spectrum of HFeCN(dmpe)<sub>2</sub> shows a very weak parent ion peak ( $m/e$  383) and a stronger  $M - 1$  ( $m/e$  382.0862 calcd vs. 382.0835 observed).
- (14) At equilibrium at 25 °C an initially 0.1 M solution of HFeNp(dmpe)<sub>2</sub> in C<sub>6</sub>D<sub>6</sub> is about 90% DFeC<sub>6</sub>D<sub>5</sub>(dmpe)<sub>2</sub> and only 10% HFeNp(dmpe)<sub>2</sub>.<sup>11</sup>
- (15) The mass spectrum of HFeCH<sub>2</sub>CN(dmpe)<sub>2</sub> shows a weak parent ion peak ( $m/e$  397) and a stronger  $M - 1$  [ $m/e$  396.099 08 vs. 396.099 1 calcd for FeCH<sub>2</sub>CN(dmpe)<sub>2</sub><sup>+</sup>]. The base peak is  $m/e$  356 [Fe(dmpe)<sub>2</sub><sup>+</sup>].
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## Iron Porphyrin Phenoxides: Models for Some Hemoglobin Mutants

E. W. Ainscough,<sup>\*1</sup> A. W. Addison,<sup>2</sup> D. Dolphin,<sup>2</sup> and B. R. James<sup>2</sup>

Contribution from the Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5. Received July 3, 1978

**Abstract:** Various substituted phenoxides (L) react with [Fe(PPIXDBE)]<sub>2</sub>O (PPIXDBE is the protoporphyrin IX di-*tert*-butyl ester dianion) to produce five-coordinate high-spin complexes Fe(PPIXDBE)L which display spectroscopic properties similar to those of the Met form of the  $\alpha$  mutant chain of HbM Boston. The addition of pyridine or 1-methylimidazole (L') to Fe(PPIXDBE)L at 77 K produced low-spin six-coordinate complexes Fe(PPIXDBE)LL' which were studied spectroscopically. With the strongly basic 2,6-dimethoxyphenoxide (L), the above reaction was studied at 298 K, where for L' = 1-methylimidazole the binding constant was approximately 100 M<sup>-1</sup> in CH<sub>2</sub>Cl<sub>2</sub>. The Fe(PPIXDBE)LL' complexes were made in an attempt to mimic the Fe(III) in the  $\alpha$  chain of Met HbM Iwate; however, the latter is high spin. With excess *p*-nitrophenoxide in CH<sub>2</sub>Cl<sub>2</sub>, Fe(PPIXDBE)(OC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>) forms Fe(PPIXDBE)(OC<sub>6</sub>H<sub>4</sub>-4-NO<sub>2</sub>)<sub>2</sub><sup>-</sup>, which exhibits a high-spin EPR spectrum at 77 K. Addition of phenoxides or fluoride to iron(II) protoporphyrin ester systems produces species such as Fe(PPIXDBE)X<sub>2</sub><sup>2-</sup> (X = OR or F), similar to those found previously with methoxide and hydroxide ions. The addition of CO to a bisphenoxy species, in Me<sub>2</sub>SO, results in a splitting of the Soret band at 438 nm into two bands at 434 and 413 nm, which are attributed respectively to a carbonyl (phenoxide) species and a carbonyl species which contains no phenoxide. The visible spectral data support the view expressed by others that upon reduction of HbM Iwate at pH 6.5 by Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> the iron-tyrosine bond is broken.

## Introduction

One class of hemoglobin mutants HbM have their iron atoms, in either the  $\alpha$  or  $\beta$  chain, permanently oxidized in vivo to Fe(III), and have the proximal or distal histidines in these chains replaced by tyrosines which are bound to the Fe(III)

[e.g., HbM Boston ( $\alpha_2$ distal His-58 $\rightarrow$ Tyr $\beta_2$ ),<sup>3</sup> HbM Iwate ( $\alpha_2$ proximal His-87 $\rightarrow$ Tyr $\beta_2$ ),<sup>4</sup> HbM Hyde Park ( $\alpha_2\beta_2$ proximal His-92 $\rightarrow$ Tyr),<sup>4</sup> and HbM Saskatoon ( $\alpha_2\beta_2$ distal His-63 $\rightarrow$ Tyr)].<sup>5</sup> In HbM Milwaukee ( $\alpha_2\beta_2$ Val-67 $\rightarrow$ Glu)<sup>6</sup> valine-67 is replaced by glutamic acid, a position four residues or one helical turn removed from the distal histidine, the glutamyl residue binding