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## Mechanism and Equilibrium Constants of the Reaction between $\eta^4$ -Heterodieneiron Tricarbonyl Complexes and Group 5 Ligands

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The complexes  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{L}$  (where  $\text{L} = \text{CO}$ ,  $\text{X} = 4\text{-NMe}_2$ ,  $4\text{-OMe}$ ,  $3\text{-OMe}$ ,  $4\text{-Me}$ ,  $4\text{-Cl}$ ;  $\text{L} = \text{SbPh}_3$ ,  $\text{X} = 3\text{-OMe}$ ,  $4\text{-Cl}$ ) and  $\text{Fe}(\text{CO})_2(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{L}$  (where  $\text{L} = \text{CO}$ ,  $\text{X} = 4\text{-NMe}_2$ ,  $4\text{-OMe}$ ,  $3\text{-OMe}$ ,  $4\text{-Me}$ ,  $4\text{-Cl}$ ;  $\text{L} = \text{PPh}_3$ ,  $\text{X} = \text{H}$ ,  $4\text{-Cl}$ ,  $4\text{-Me}$ ,  $4\text{-OMe}$ ,  $3\text{-OMe}$ ) have been prepared and characterized. The reaction between  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  (where  $\text{X} = \text{H}$ ,  $3\text{-OMe}$ ,  $4\text{-Cl}$ ) and  $\text{SbPh}_3$  has been studied and the equilibrium constants and forward and reverse rate constants for this reaction have been measured. From the results obtained, it is concluded that the mechanism of this reaction proceeds via a dissociative equilibrium of the  $\eta^4$  complexes to  $\eta^2$  unsaturated complexes. The reaction between  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  (where  $\text{X} = \text{H}$ ,  $4\text{-NMe}_2$ ,  $3\text{-OMe}$ ,  $4\text{-OMe}$ ,  $4\text{-Me}$ ,  $4\text{-Cl}$ ) and  $\text{PPh}_3$  has also been studied. The kinetic law, the activation parameters, and the substituent effect indicate a reaction mode proceeding in two parallel directions. One of these is the same as that found for  $\text{SbPh}_3$  and the other corresponds to an associative process with the phosphine ligand. These results may be generalized to other diene complexes of iron tricarbonyl.

### Introduction

There are several literature reports of mechanistic studies on the reactivity of metal carbonyl complexes containing bidentate ligands, in most of which the bidentate ligands involved form bonds to the metal which are almost independent of one another.<sup>1-4</sup> By way of contrast, the complexes  $\text{M}(\text{CO})_n(\eta^4\text{-diene})$  ( $\text{M} = \text{Mo}$ ,  $\text{Fe}$ , etc.) are sandwich systems with a delocalized iron-ligand bond. They are very important intermediates in the reactions of organic compounds with metal carbonyls.<sup>5</sup>

Unfortunately, the complexes with iron are very inert in nonpolar solvents and only at temperatures higher than 120 °C do they react with group 5 ligands (such as phosphines). There is only a single study on the reaction mechanism of such complexes,<sup>6</sup> but the results were not conclusive.  $[\text{Fe}(\text{CO})_3(\eta^4\text{-heterodiene})]$  complexes are much more reactive than their diene analogues<sup>7,8</sup> and kinetic studies may be carried out in relatively mild conditions.

We previously reported results on the products of the reaction between  $\text{Fe}(\text{CO})_3(\eta^4\text{-PhCH}=\text{CHCOR})$  complexes and group 5 ligands.<sup>9</sup> The present article describes the results of a detailed study of the mechanism of this reaction; this forms the basis for an investigation of the reactivity of  $\text{Fe}(\text{CO})_3(\eta^4\text{-diene})$  complexes, which will thus allow us to arrive at a complete picture of the reactivity of these iron carbonyls.

### Experimental Section

**General Data.** All reactions involving organometallic complexes were carried out under a dry nitrogen atmosphere. The acetone was

a commercial product (Carlo Erba, Milan) and was used without further purification. The benzene was purified by distillation over metallic sodium and the ethyl ether by distillation over  $\text{LiAlH}_4$ . Dichloromethane was heated at reflux over  $\text{P}_2\text{O}_5$ , and acetonitrile (AN) was purified as described in the literature.<sup>10</sup>

NMR spectra were obtained on  $\text{CS}_2$  solutions using a Jeol C-60HL spectrometer with TMS as reference. IR spectra were registered on Perkin-Elmer IR 521 and 257 spectrophotometers using 0.5-mm NaCl cells.

**Preparations.**  $\text{C}_6\text{H}_4\text{XCH}=\text{CHCHO}$ . The compounds with  $\text{X} = \text{H}$ ,  $4\text{-NMe}_2$ , and  $2\text{-NO}_2$  were commercial products (Fluka, CH-9470 Buchs). Those with  $\text{X} = 4\text{-Cl}$ ,  $3\text{-Cl}$ ,  $3\text{-OMe}$ ,  $4\text{-OMe}$ ,  $4\text{-Me}$ , and  $3\text{-NO}_2$  were prepared from the corresponding acids,  $\text{C}_6\text{H}_4\text{XCH}=\text{CHCO}_2\text{H}$ , available commercially (Fluka). The acids were reduced to alcohols as follows.  $\text{LiAlH}_4$  (in 0.6:1 mole ratio with respect to the acid) was added with stirring to 50 mL of diethyl ether in a three-necked flask and the mixture cooled to 0 °C. A diethyl ether solution was then added, dropwise with stirring (for acids only slightly soluble in diethyl ether, the reaction was carried out on the acid suspended in 500 mL of ether). The reaction was allowed to continue for ca. 1 h and the alcohol obtained separated using the usual workup procedures.<sup>11</sup> Yields were 70-80%, except for the derivative having  $\text{X} = 3\text{-NO}_2$ , the low solubility of which in diethyl ether greatly lowered the yield.

The alcohols were oxidized to aldehydes using  $\text{CrO}_3(\text{py})_2$ , prepared as described in the literature.<sup>12</sup> The oxidations were carried out using the procedures of ref 12. The products obtained by crystallization from *n*-hexane were all low-melting solids; yields ca. 70%.

$\text{Fe}(\text{CO})_4(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$ . Equimolar quantities of  $\text{C}_6\text{H}_4\text{XCH}=\text{CHCHO}$  and  $\text{Fe}_2(\text{CO})_9$ <sup>13</sup> were allowed to react in deaerated benzene at 12-15 °C until the  $\text{Fe}_2(\text{CO})_9$  crystals were consumed. The reaction times varied from 10 h to 2 days, depending

Table I. CO Stretching Frequencies of  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{L}$

X	L	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$	$\nu_{\text{CO}}$ , $\text{cm}^{-1}$	Solvent
H	CO	2100, 2096, 2039, 2027, 2020, 2000	1690, 1681	<i>n</i> -Hexane
H	PPh <sub>3</sub>	2041, 1973		Acetone
4-NMe <sub>2</sub>	PPh <sub>3</sub>	2093, 2088, 2031, 2015, 2010, 1992	1685	<i>n</i> -Hexane
4-NMe <sub>2</sub>	SbPh <sub>3</sub>	2030, 1960		Acetone
4-NMe <sub>2</sub>	PPh <sub>3</sub>	2047, 1968		Acetone
3-OMe	CO	2097, 2091, 2036, 2024, 2016, 1997	1691, 1679	<i>n</i> -Hexane
3-OMe	SbPh <sub>3</sub>	2036, 2029, 1972		<i>n</i> -Hexane
3-OMe	PPh <sub>3</sub>	2048, 1973		Acetone
3-OMe	P( <i>n</i> -Bu) <sub>3</sub>	2031, 1961		Acetone
4-OMe	CO	2099, 2094, 2038, 2026, 2019, 1999	1695, 1684	<i>n</i> -Hexane
4-OMe	SbPh <sub>3</sub>	2037, 1967		Acetone
4-Cl	CO	2096, 2091, 2036, 2023, 2017, 1998	1685	<i>n</i> -Hexane
4-Cl	SbPh <sub>3</sub>	2042, 2034, 1971		<i>n</i> -Hexane
4-Cl	PPh <sub>3</sub>	2046, 1968		Acetone
4-Me	CO	2099, 2094, 2038, 2025, 2019, 1999	1694, 1682	<i>n</i> -Hexane
4-Me	SbPh <sub>3</sub>	2040, 1971		Acetone
3-NO <sub>2</sub>	CO	2096, 2036, 2012		<i>n</i> -Hexane
2-NO <sub>2</sub>	CS <sub>2</sub>	2098, 2047, 2026, 2009	1682	CS <sub>2</sub>

<sup>a</sup> CO stretching of the aldehyde ligands.

on the aldehyde. At the end of reaction, small quantities of the complexes  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  were formed. The solution was filtered and dried and the solid crystallized from an *n*-hexane-dichloromethane mixture to give yellow crystals.

The complexes so prepared were those with X = 4-NMe<sub>2</sub>, 4-Cl, 4-OMe, 2-OMe, and 4-Me. The complexes with X = 3-NO<sub>2</sub> and 2-NO<sub>2</sub> could not be purified.

$\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$ . Equimolar quantities of  $\text{Fe}_2(\text{CO})_9$  and ligand were allowed to react in deaerated benzene at 35–50 °C for times varying from 5 to 20 h. For X = 4-OMe, the reaction was carried out at 15 °C because of the greater instability of the complex. When the reaction had gone to completion, the solution was filtered and dried. Excess ligand was removed by column chromatography on neutral Al<sub>2</sub>O<sub>3</sub> using *n*-hexane-dichloromethane as eluent.

$\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{SbPh}_3$ . Complexes with X = H, 4-Cl, and 3-OMe were isolated as follows. About 0.5 g of  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  and 1.5 g of SbPh<sub>3</sub> were dissolved in 10 mL of deaerated acetone at room temperature. The reaction reached equilibrium after 3 h. The solution was evaporated to dryness and the solid chromatographed on a neutral Al<sub>2</sub>O<sub>3</sub> column using 2:3 (v/v) dichloromethane-*n*-hexane as eluent. Of the two bands formed, the faster (red) corresponded to the reagent complex, and the slower (yellow) to the complex  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{SbPh}_3$ . When the two bands had become well separated, the column was broken and the yellow compound extracted with acetone and dried (yield ca. 50%). The compound was further purified by crystallization from a dichloromethane-*n*-hexane mixture at -20 °C.

An alternative method exploits the lower solubility of  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{SbPh}_3$  compared with that of  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$ , as follows.  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  (0.5 g) and SbPh<sub>3</sub> (1.5 g) were dissolved in 10 mL of deaerated ethyl ether. The solution was left to react at room temperature for 4 h, and then concentrated to one-third of the initial volume, and left to crystallize at -20 °C. Crystals of pure  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{SbPh}_3$  were obtained, although in low yield (10–20%).

$\text{Fe}(\text{CO})_2(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{PPh}_3$ .  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  (3 g) and PPh<sub>3</sub> (2.8 g) were allowed to react in deaerated benzene (100 mL) for 30 min at 71 °C. The benzene solution was cooled and a large quantity of  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$  separated. The solution remaining after filtration was evaporated to dryness and the solid extracted with *n*-hexane. The *n*-hexane solution (which did not contain  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ ) was concentrated and left to crystallize. The first fraction contained the ligand; the second gave red crystals of  $\text{Fe}(\text{CO})_2(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{PPh}_3$  (yield ca. 20%).

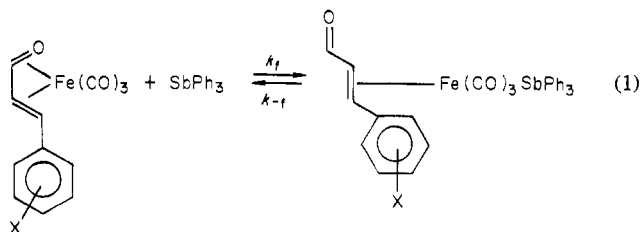
**Equilibrium Constants.** The equilibrium constants for the reaction between  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  and SbPh<sub>3</sub> were measured in acetone at temperatures between -20 and +20 °C. In AN the complexes decompose, and in the other solvents measurements could be performed only at +20 °C. For temperatures lower than 10 °C, thermostating was obtained using a cryostat ( $\pm 0.2$  °C). Concentration ratios  $[\text{SbPh}_3]/[\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})]$  were at least 50:1, so that SbPh<sub>3</sub> concentrations may be considered constant and equal to the initial concentration.

The equilibrium concentrations of the complexes were measured from the absorbances of the CO stretching bands of the reagent complexes, and those of the products, after verifying that these followed Beer's law. Measurements were repeated at least three times at different concentrations of SbPh<sub>3</sub>. The results were reproducible to less than  $\pm 5\%$ .

The equilibrium constants were measured only for the complexes with X = H, 3-OMe, and 4-Cl, because the successive reactions in the other complexes were very fast, and this did not allow equilibrium to be reached.

**Rate Constants.** Reactions were carried out in a closed container, immersed in a thermostated bath ( $\pm 0.1$  °C), fitted with a rubber stopper through which aliquots were withdrawn with a syringe at chosen times. The concentrations were measured from the intensities of the CO stretching band in the complexes.

(a) **Reaction with SbPh<sub>3</sub>.** The stoichiometry of the reaction is



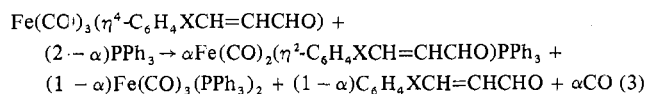
For X = H, 3-OMe, and 4-Cl, both rate constants,  $k_f$  and  $k_{-f}$ , were measured. The rate constants  $k_f$  were measured as follows. With a large excess of SbPh<sub>3</sub> (50:1) compared to the concentration of the reagent complex, the reaction may be considered to be pseudo first order, with  $k_1 = k_f[\text{SbPh}_3]$ . Under these conditions, reaction 1 may be considered a first-order equilibrium in both the forward and the reverse direction. The kinetics of such a reaction is expressed by the equation<sup>14</sup>

$$\ln(D_0 - D_e)/(D_t - D_e) = k_1(C_0/x_e)t \quad (2)$$

in which  $D_0$ ,  $D_t$ , and  $D_e$  represent the higher frequency CO stretching absorption of the reagent complex at the beginning of the reaction, at time  $t$ , and at equilibrium, respectively;  $C_0$  is the initial concentration of the  $\eta^4$  complex, and  $x_e$  the equilibrium concentration of the  $\eta^2$  complex (measured experimentally).

The rate constants  $k_{-f}$  are readily measured, since reaction 1 is shifted completely toward the reagent complexes in the absence of excess SbPh<sub>3</sub>. This reaction is first order in the  $\eta^2$  complex and the rate constants were measured from  $\ln(D_0/D_t) = k_{-f}t$ , in which  $D_0$  and  $D_t$  represent the absorbances of the lower frequency CO stretching band of the  $\eta^2$  complex at the beginning of reaction and at time  $t$ . The same results were obtained by following the appearance of the  $\eta^4$  complexes with time.

(b) **Reaction with PPh<sub>3</sub>.** The stoichiometry of the reaction is



where  $\alpha$  is the fraction of  $\text{Fe}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{PPh}_3$  per mole of reagent complex.

Reaction 3 was studied for the substituents X = H, 4-NMe<sub>2</sub>, 4-OMe, 3-OMe, 4-Me, and 4-Cl. At temperatures higher than 20 °C, no formation of the intermediates  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{L}$  (the final products of the reaction with SbPh<sub>3</sub>) was observed. However, at lower temperatures and very high PPh<sub>3</sub> concentration ( $> 5 \times 10^{-1}$  M) the formation of these complexes was observed spectroscopically.

Reactions were carried out in the temperature range 30–50 °C, using a large excess of ligand ( $> 10:1$ ). Kinetics were followed up

Table II. CO Stretching Frequencies of  $\text{Fe}(\text{CO})_2(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{L}$ 

X	L	$\nu_{\text{CO}}, \text{cm}^{-1}$	Solvent
H	CO	2074, 2010, 1992	<i>n</i> -Hexane
H	PPh <sub>3</sub>	1998, 1937	Acetone
4-NMe <sub>2</sub>	CO	2065, 2007, 1987	<i>n</i> -Hexane
4-NMe <sub>2</sub>	PPh <sub>3</sub>	1992, 1932	Acetone
3-OMe	CO	2077, 2019, 1998	<i>n</i> -Hexane
3-OMe	PPh <sub>3</sub>	2000, 1940	Acetone
3-OMe	P( <i>n</i> -Bu) <sub>3</sub>	1990, 1925	Acetone
4-OMe	CO	2073, 2014, 1992	<i>n</i> -Hexane
4-OMe	PPh <sub>3</sub>	1997, 1937	Acetone
4-Cl	CO	2078, 2020, 1998	<i>n</i> -Hexane
4-Cl	PPh <sub>3</sub>	1998, 1938	Acetone
4-Me	CO	2076, 2018, 1997	<i>n</i> -Hexane
4-Me	PPh <sub>3</sub>	1996, 1936	Acetone
3-NO <sub>2</sub>	CO	2075, 2029, 2018	<i>n</i> -Hexane
2-NO <sub>2</sub>	CO	2083, 2034	CH <sub>2</sub> Cl <sub>2</sub>

to ca. 90% completion (ca. 3 half-lives). Rate constants were measured by following the disappearance of the highest frequency CO stretching band of the reagent complexes, using the expression  $\ln(D_0/D_t) = k_{\text{obsd}}t$ , in which  $D_0$  and  $D_t$  are the absorbances of this band at zero time and at time  $t$ . The constants could not be measured by following the appearance of the reaction products (e.g.,  $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$ ) because  $\ln [D_{\infty}/(D_{\infty} - D_t)] = k_{\text{obsd}}t$ , in which  $D_t$  and  $D_{\infty}$  are the absorbances of the products at time  $t$  and at the end of reaction, is not linear.

### Results and Discussion

(a) **Structure of the Complexes.** The structure of the complexes could be deduced from the IR and NMR spectra. The CO stretching frequencies of the complexes  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{L}$  (L = CO, SbPh<sub>3</sub>, P(*n*-Bu)<sub>3</sub>, PPh<sub>3</sub>) are listed in Table I. The CO stretching frequencies of the complexes  $\text{Fe}(\text{CO})_2(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{L}$  (L = CO, PPh<sub>3</sub>, P(*n*-Bu)<sub>3</sub>) are listed in Table II. Table III gives the <sup>1</sup>H NMR shifts of the complexes  $\text{Fe}(\text{CO})_4(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  and  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$ . The former complexes show four absorption bands<sup>15</sup> in the 2100–1980-cm<sup>-1</sup> region in polar and polarizable solvents, as does the complex with X = H, the spectrum of which has been reported elsewhere.<sup>16</sup>

In inert solvents (e.g., *n*-hexane, CS<sub>2</sub>) these bands split into doublets, and this has been attributed to the presence of two conformers, arising because of two possible arrangements of the CHO group with respect to the olefinic bond (*s*-cis and

*s*-trans).<sup>17</sup> The ratio of the integrated band intensities of the bands at higher frequency (e.g., for X = H, the band at 2100 cm<sup>-1</sup> attributed to the *s*-cis conformer<sup>18</sup> and the band at 2096 cm<sup>-1</sup> attributed to *s*-trans conformer) decreases with increase in the donor power of the substituent X.

The four CO stretching bands of the tetracarbonyliron complexes are explained on the basis of a pseudo-C<sub>2v</sub> symmetry, derived from a trigonal-bipyramidal structure having the olefinic bond in the equatorial plane of the bipyramid, as found with other olefinic ligands,<sup>19</sup> and confirmed by recent calculations.<sup>20</sup> This structure is confirmed by the NMR spectra, which, compared to those of the free ligands, show a marked shift to higher fields of the chemical shifts of the protons H<sub>a</sub> and H<sub>b</sub> (Table III) due to coordination to the metal, while the chemical shift of proton H<sub>c</sub> changes little from that in the free ligand.

The two protons H<sub>a</sub> and H<sub>b</sub> comprise an AB system and appear as a quartet, in which the two bands at higher field (due to H<sub>b</sub>) are further doubled due to coupling with proton H<sub>c</sub>. The effect of the substituent X on the chemical shifts is small and lies within experimental error.

In polar or polarizable solvents the complexes  $\text{Fe}(\text{CO})_3(\eta^2\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})\text{SbPh}_3$  give two stretching bands in the IR with intensities of the lower frequency band much higher than those of that at higher frequency. In inert solvents, a shoulder appears on the higher frequency band, which may be due to the presence of two conformers, as in the corresponding tetracarbonyliron complexes.<sup>17,18</sup> On the basis of the softness and hardness of the ligands, the structure of these complexes is probably trigonal bipyramidal, with the olefinic  $\pi$ -acceptor substituent lying in the equatorial plane of the trigonal bipyramid and the  $\sigma$ -donor substituent, SbPh<sub>3</sub>, in the apical position.<sup>21</sup> This would give a molecule of C<sub>s</sub> symmetry with three CO stretching bands. The number of experimental CO stretchings is 2 and the intensity ratio between them is better explained by a molecule of C<sub>3v</sub> symmetry, i.e., a trigonal-bipyramidal structure in which the olefinic substituents and SbPh<sub>3</sub> lie in apical positions. This conclusion is in contrast with the behavior of the trigonal-bipyramidal complexes<sup>20</sup> in which the  $\pi$ -acceptor substituents (e.g., olefins) prefer the equatorial position.

The structure of the complexes  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  is similar to that found for the

Table III. NMR Spectra in CS<sub>2</sub> of  $\text{Fe}(\text{CO})_4(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  (I) and  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$  (II)<sup>a</sup>

X	I					II					
	$\tau_{\text{H}_a}$	$\tau_{\text{H}_b}$	$\tau_{\text{H}_c}$	$\tau_{\text{X}}$	$J_{bc}$	$J_{ab}$	$\tau_{\text{H}_a}$	$\tau_{\text{H}_b}$	$\tau_{\text{H}_c}$	$\tau_{\text{X}}$	$J_{ab}$
4-OMe	5.23	5.77	1.04	6.37	4.5	10.8	4.13	6.87	2.60	6.35	9.9
4-Cl	5.29	5.83	0.90	7.80	3.3	10.5	4.10	6.96	2.53	6.35	10.0
4-Me	5.26	5.81	1.03	7.80	3.0	11.4	4.08	6.89	2.58	7.78	9.1
3-OMe	5.27	5.82	0.71	5.71	4.35	11.3	4.07	6.95	2.55	6.33	9.3
4-NMe <sub>2</sub>							4.16	6.82	2.65	7.10	8.7

<sup>a</sup>  $\tau$  in ppm;  $J$  in Hz.

Table IV. Rate Constants and Equilibrium Constants for the Reaction between  $\text{Fe}(\text{CO})_3(\eta^4\text{-C}_6\text{H}_4\text{XCH}=\text{CHCHO})$ <sup>a</sup> and SbPh<sub>3</sub><sup>b</sup>

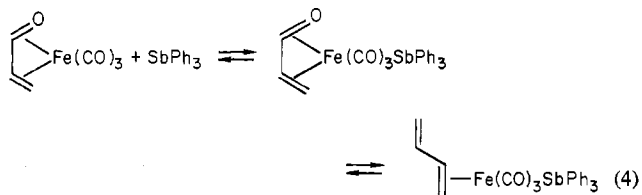
X	Solvent	T, °C	10 <sup>3</sup> k <sub>f</sub> , s <sup>-1</sup>	10 <sup>5</sup> k <sub>-f</sub> , s <sup>-1</sup>	k <sub>f</sub> /k <sub>-f</sub> , M <sup>-1</sup>	K <sub>eq</sub> , M <sup>-1</sup>
H	Acetone <sup>c</sup>	20	0.72 ± 0.01	7.7 ± 0.1	9.47 ± 0.06	10.4 ± 0.2
H	Benzene	20	0.77 ± 0.02	11.9 ± 0.2	6.50 ± 0.10	6.80 ± 0.1
H	CH <sub>2</sub> Cl <sub>2</sub>	20	0.50 ± 0.01	4.9 ± 0.1	10.1 ± 0.1	9.55 ± 0.05
H	Et <sub>2</sub> O	20	0.78 ± 0.05	13.3 ± 0.2	5.85 ± 0.20	6.70 ± 0.15
3-OMe <sup>d</sup>	Acetone	20	0.83 ± 0.02	7.5 ± 0.1	10.75 ± 0.15	16.5 ± 0.5
3-OMe <sup>d</sup>	Acetone	0	0.107 ± 0.005	0.33 ± 0.01	32.90 ± 0.2	40.5 ± 1.5
4-Cl <sup>e</sup>	Acetone	20	0.88 ± 0.03	7.2 ± 0.3	12.2 ± 0.2	17.1 ± 0.3
4-Cl <sup>e</sup>	Acetone	0	0.097 ± 0.005	0.25 ± 0.01	38.8 ± 1.5	46.5 ± 1.5

<sup>a</sup> Concentration of the complex in the range (3–7) × 10<sup>-3</sup> M. <sup>b</sup> Concentration of the ligand in the range (0.9–4) × 10<sup>-1</sup> M. <sup>c</sup> Values from ref 9. <sup>d</sup>  $\Delta H = -7.03 \pm 0.5$  kcal/mol,  $\Delta S = -29 \pm 2$  eu,  $\Delta H_{\text{f}}^{\ddagger} = 16 \pm 1$  kcal/mol,  $\Delta S_{\text{f},293}^{\ddagger} = -22 \pm 3$  eu,  $\Delta H_{\text{f}}^{\ddagger} = 24 \pm 1$  kcal/mol,  $\Delta S_{\text{f},293}^{\ddagger} = 0 \pm 3$  eu. <sup>e</sup>  $\Delta H = -8.0 \pm 0.6$  kcal/mol,  $\Delta S = -32 \pm 2$  eu,  $\Delta H_{\text{f}}^{\ddagger} = 17 \pm 1$  kcal/mol,  $\Delta S_{\text{f},293}^{\ddagger} = -15 \pm 3$  eu,  $\Delta H_{\text{f}}^{\ddagger} = 26 \pm 1$  kcal/mol,  $\Delta S_{\text{f},293}^{\ddagger} = -10 \pm 3$  eu.

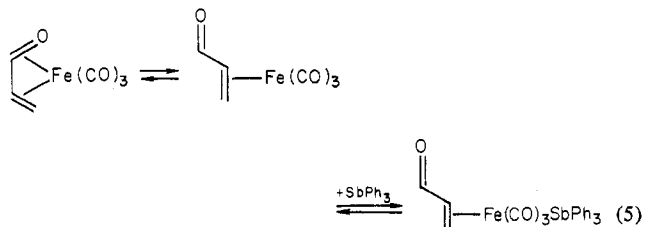
complex with  $X = H$ ,<sup>15</sup> having known crystal structure.<sup>22</sup> The substituents  $X$  do not sensibly change this structure, as is confirmed by both IR (Table II) and NMR (Table III) spectra. The substitution of a CO group by a ligand  $L$  (e.g.,  $PPh_3$ ) presents some problems as regards the symmetry. The structural data for  $Fe(CO)_3(\eta^4-C_6H_5CH=CHCHO)$ ,<sup>21</sup> which are similar to those for  $Fe(CO)_3(\eta^4-CH_2=CHCH_2)$ ,<sup>23</sup> indicate a square-pyramidal structure with the diene ligand and two CO groups occupying the four basal positions and with the other CO at the apex of the pyramid. In the complexes  $Fe(CO)_2(\eta^4-C_6H_4XCH=CHCHO)L$  it is not possible to decide whether  $L$  occupies the apical or the basal position of the square pyramid.

**(b) Reaction Mechanisms. Reaction with  $SbPh_3$ .** The equilibrium constants and the rate constants  $k_f$  and  $k_r$  for reaction 1, in several solvents and at various temperatures, together with thermodynamic and activation parameters, are shown in Table IV.

The forward reaction is first order in complex and in ligand ( $SbPh_3$ ). These results do not allow a reaction mechanism to be identified. Thus, both the associative process



and the dissociative process



would give a kinetic law following the experimentally observed order.

The effect of the substituent may be utilized to discriminate between the two mechanisms, although the only small differences in the electronic effects in the substituents studied ( $X = H, 3\text{-OMe}, 4\text{-Cl}$ ) do not allow this to be done unequivocally. The solvent exerts an appreciable effect and the  $k_f$  and  $k_r$  values both follow the order benzene  $\gg$  acetone  $\gg$   $\text{CH}_2\text{Cl}_2$ . This order indicates that neither the dielectric constant nor the dipole moment is the dominant factor, but, instead, the ability of the solvent to make  $\pi$  electrons (benzene) or  $\sigma$  electrons (e.g., ether) available. This fact induces us to prefer the dissociative mechanism (5), since the intermediate unsaturated species would be stabilized by the solvent.

The thermodynamic results obtained for reaction 1 are in agreement with the results of ref 9. The effect of substituents on the equilibrium constants follows the order  $4\text{-Cl} \sim 3\text{-OMe} > H$ , indicating that electron-attracting substituents stabilize the complexes  $Fe(CO)_3(\eta^2-C_6H_4XCH=CHCHO)SbPh_3$ . The solvent influences these constants in the order acetone  $\gg$   $\text{CH}_2\text{Cl}_2 \gg$  benzene  $\sim$   $\text{Et}_2\text{O}$ . This order is that of decreasing dielectric constant and indicates that the effects are due to the greater polarity of the  $\eta^2$  complexes compared to the  $\eta^4$  ones. There is still not sufficient information to unravel the mechanism, and the reaction with  $PPh_3$  was studied as a further aid in doing this.

**Reaction with  $PPh_3$ .** All the kinetics are pseudo first order in the complex and the  $k_{\text{obsd}}$  values vary with ligand con-

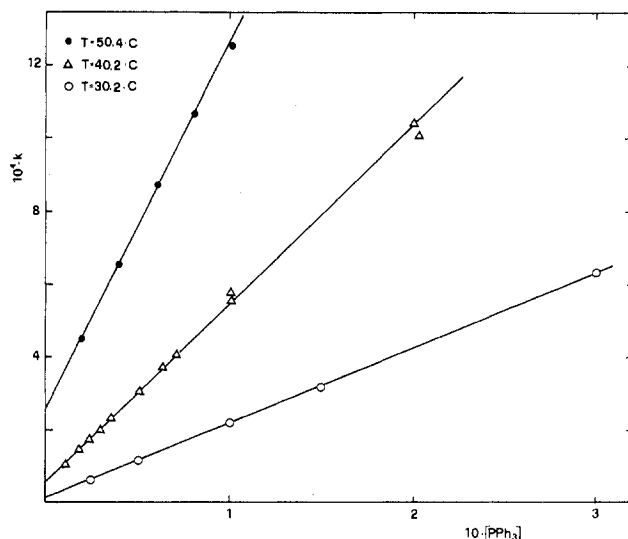


Figure 1.  $k_{\text{obsd}}$  vs.  $[PPh_3]$  for the reaction of  $Fe(CO)_3(\eta^4-3\text{-OMeC}_6\text{H}_4\text{CH=CHCHO})$  and  $PPh_3$  in acetone.

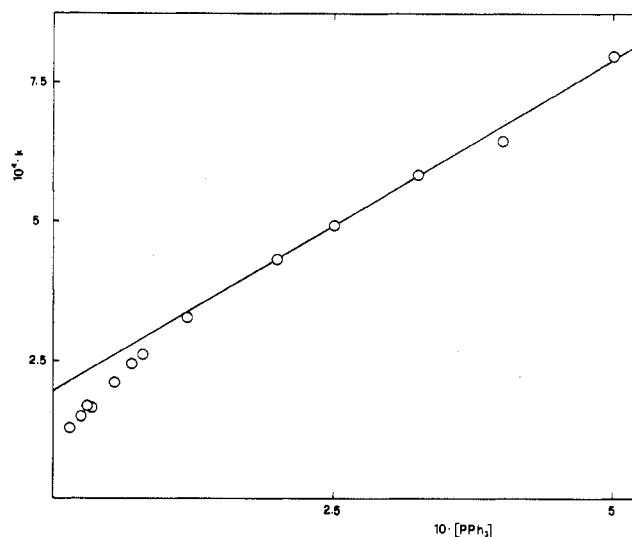
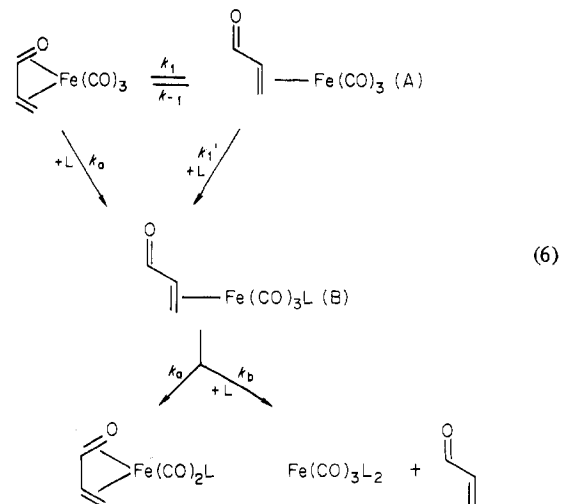


Figure 2.  $k_{\text{obsd}}$  vs.  $[PPh_3]$  for the reaction of  $Fe(CO)_3(\eta^4-4\text{-NMe}_2\text{C}_6\text{H}_4\text{CH=CHCHO})$  and  $PPh_3$  in acetone at  $40.2^\circ\text{C}$ .

centrations. Plots of  $k_{\text{obsd}}$  vs.  $[PPh_3]$  are linear (e.g.,  $X = 3\text{-OMe}$ , Figure 1) for all the substituents studied, except for  $X = 4\text{-NMe}_2$  (see Figure 2).

A mechanism explaining all the experimental facts is given by (6). Applying the steady-state approximation to the



$\eta^4$ -Heterodieneiron Tricarbonyl Complexes

intermediates A and B, the following kinetic law is obtained

$$-\frac{dC}{dt} = \frac{k_1 k_1' [L][C]}{k_{-1} + k_1' [L]} + k_a [L][C] \quad (7)$$

Equation 7 gives

$$k_{\text{obsd}} = \frac{k_1 k_1' [L]}{k_{-1} + k_1' [L]} + k_a [L] \quad (8)$$

In limit  $k_1' [L] \gg k_{-1}$ ,  $k_{\text{obsd}} = k_1 + k_a [L]$  (intercept =  $k_1$ ); this is the case of Figure 1.

When  $k_{-1} \approx k_1' [L]$ , from (8)

$$k_{\text{obsd}} - k_a [L] = \frac{k_1 k_1' [L]}{k_{-1} + k_1' [L]} \quad (9)$$

and

$$\frac{1}{k_{\text{obsd}} - k_a [L]} = \frac{k_1}{k_1 k_1' [L]} + \frac{1}{k_1} \quad (10)$$

This situation is indicated in Figure 3 for X = 4-NMe<sub>2</sub>. In this case the intercept is  $1/k_1$  and

$$\text{slope/intercept} = \frac{k_{-1}}{k_1 k_1'} k_1 = \frac{k_{-1}}{k_1'} \quad (11)$$

The mechanism proposed above thus explains all the experimental results. The fact that the appearance of products does not follow a pseudo-first-order law may be due to the circumstance that the intermediate B does not obey the steady-state approximation. Indeed, under certain experimental conditions (temperature <20 °C and  $[PPh_3] > 5 \times 10^{-1}$  M), this intermediate may be observed spectroscopically. In this case, the effect of a slow stage of reaction would make itself felt only on the formation rate of the products and not on the rate of disappearance of the reagents.

The kinetic data of the various substituents, i.e.,  $k_1$ ,  $k_a$ , and  $k_{-1}/k_1'$ , are listed in Table V.

Further confirmation of mechanism (6) is obtained by examining the activation parameters (Table V). Thus, the dissociative process gives high  $\Delta H_1^\ddagger$  values and positive  $\Delta S_1^\ddagger$  values, while the associative process gives low  $\Delta H_a^\ddagger$  values and negative  $\Delta S_a^\ddagger$  values, as predicted.

The effect of the substituent further supports the mechanism proposed. Substituent X influences little  $k_a$  (maximum variation 2). Electron-donor substituents decrease this value, as expected, because of the increase (by ca. 20 times) of the rate constants  $k_1$ , because they destabilize the complex  $Fe(CO)_3(\eta^4-C_6H_4XCH=CHCHO)^{24}$  and thus increase the dissociation rate. Since the substituent X is closer to the dissociation center, the effect is more accentuated compared to that in the associative process.

### Conclusions

Summarizing the above results, the mechanism (6) for L = PPh<sub>3</sub> is supported by (a) the kinetic law, which explains all the experimental facts, (b) evidence of the formation of the intermediate  $Fe(CO)_3(\eta^2-C_6H_4XCH=CHCHO)PPh_3$ , (c) the values of the activation parameters, and (d) the effect of the substituent X on the rate constant  $k_1$  and  $k_a$ .

The results obtained for L = PPh<sub>3</sub> may be extended to L = SbPh<sub>3</sub>. Since the latter ligand is much less nucleophilic than PPh<sub>3</sub>,  $k_a$  is much smaller than  $k_1$ , and it is reasonable to conclude that the only reaction mode operating is that of scheme (5).

This dissociative mechanism requiring a rapid dissociative mechanism

$$\eta^4 \rightleftharpoons \eta^2 \quad (12)$$

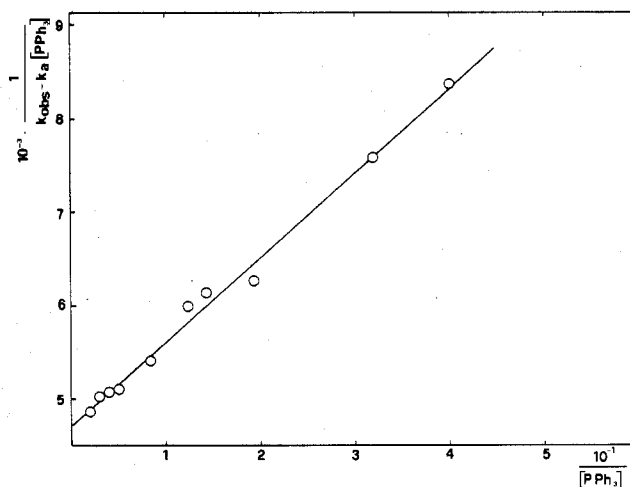


Figure 3.  $1/(k_{\text{obsd}} - k_a [PPh_3])$  vs.  $[PPh_3]$  for the reaction of  $Fe(CO)_3(\eta^4-4-NMe_2-C_6H_4CH=CHCHO)$  and  $PPh_3$  in acetone at 40.2 °C.

Table V. Summary of the Kinetic Results for Reaction 3 in Acetone

T, °C	X	$10^4 k_1$ , s <sup>-1</sup>	$10^3 k_a$ , M <sup>-1</sup> s <sup>-1</sup>	$10^2 k_{-1}/k_1'$
40.2	4-Cl	0.70	5.38	
50.4	3-OMe <sup>a</sup>	2.50	10.20	
40.2	3-OMe <sup>a</sup>	0.55	4.85	
30.2	3-OMe <sup>a</sup>	0.12	2.07	
40.2	H	1.15	4.24	
40.2	4-Me	1.15	4.32	
40.2	4-OMe	1.10	4.46	
30.2	4-NMe <sub>2</sub>	2.13	1.18	1.92

<sup>a</sup> The activation parameters for substituents are as follows: first-order process,  $\Delta H_1^\ddagger = 29.2 \pm 1$  kcal/mol,  $\Delta S_1^\ddagger_{313.3} K = 15 \pm 3$  eu; second-order process,  $\Delta H_a^\ddagger = 15 \pm 1$  kcal/mol,  $\Delta S_a^\ddagger_{313.2} K = -22 \pm 3$  eu.

known to occur in heterodieneiron tricarbonyl complexes, may be considered a general reaction mode for all diene derivatives of iron tricarbonyl. This is supported by recent studies on the thermolysis of  $Fe(CO)_3(\eta^4\text{-diene})$  complexes,<sup>25</sup> in which the isomerization observed was explained as being due to the formation of unsaturated  $\eta^2$ -bonded intermediates. This mechanism may also be invoked to explain the reaction of  $Fe(CO)_3(\eta^4\text{-diene})$  complexes with group 5 ligands. This reaction does not take place below 120 °C, probably because the dissociative equilibrium (5) is strongly shifted to the left.

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**Registry No.**  $Fe(CO)_3(\eta^2-C_6H_5CH=CHCHO)CO$ , 63700-23-2;  $Fe(CO)_3(\eta^2-C_6H_5CH=CHCHO)PPh_3$ , 56556-29-7;  $Fe(CO)_3(\eta^2-4-NMe_2-C_6H_4CH=CHCHO)CO$ , 63625-80-9;  $Fe(CO)_3(\eta^2-4-NMe_2-C_6H_4CH=CHCHO)SbPh_3$ , 63625-81-0;  $Fe(CO)_3(\eta^2-4-NMe_2-C_6H_4CH=CHCHO)PPh_3$ , 63625-82-1;  $Fe(CO)_3(\eta^2-3-OMe-C_6H_4CH=CHCHO)CO$ , 63625-83-2;  $Fe(CO)_3(\eta^2-3-OMe-C_6H_4CH=CHCHO)SbPh_3$ , 63625-84-3;  $Fe(CO)_3(\eta^2-3-OMe-C_6H_4CH=CHCHO)PPh_3$ , 63625-85-4;  $Fe(CO)_3(\eta^2-3-OMe-C_6H_4CH=CHCHO)P(n-Bu)_3$ , 63625-86-5;  $Fe(CO)_3(\eta^2-4-OMe-C_6H_4CH=CHCHO)CO$ , 63625-87-6;  $Fe(CO)_3(\eta^2-4-OMe-C_6H_4CH=CHCHO)SbPh_3$ , 63625-88-7;  $Fe(CO)_3(\eta^2-4-Cl-C_6H_4CH=CHCHO)CO$ , 63625-89-8;  $Fe(CO)_3(\eta^2-4-Cl-C_6H_4CH=CHCHO)SbPh_3$ , 63625-90-1;  $Fe(CO)_3(\eta^2-4-Cl-C_6H_4CH=CHCHO)PPh_3$ , 63625-91-2;  $Fe(CO)_3(\eta^2-4-Me-C_6H_4CH=CHCHO)CO$ , 63625-92-3;  $Fe(CO)_3(\eta^2-4-Me-C_6H_4CH=CHCHO)SbPh_3$ , 63625-67-2;  $Fe(CO)_3(\eta^2-3-NO_2-C_6H_4CH=CHCHO)CO$ , 63625-68-3;  $Fe(CO)_3(\eta^2-2-NO_2-C_6H_4CH=CHCHO)CS_2$ , 63625-69-4;  $Fe(CO)_2(\eta^4-C_6H_5CH=CHCHO)CO$ , 38720-33-1;  $Fe(CO)_2(\eta^4-C_6H_5CH=CHCHO)PPh_3$ ,

63625-70-7;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-NMe}_2\text{-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{CO}$ , 63625-71-8;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-NMe}_2\text{-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{PPh}_3$ , 63625-72-9;  $\text{Fe}(\text{CO})_2(\eta^4\text{-3-OMe-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{CO}$ , 63625-73-0;  $\text{Fe}(\text{CO})_2(\eta^4\text{-3-OMe-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{PPh}_3$ , 63625-74-1;  $\text{Fe}(\text{CO})_2(\eta^4\text{-3-OMe-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{P}(n\text{-Bu})_3$ , 63625-75-2;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-OMe-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{CO}$ , 63625-76-3;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-OMe-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{PPh}_3$ , 63625-77-4;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-Cl-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{CO}$ , 63641-40-7;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-Cl-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{PPh}_3$ , 63625-78-5;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-Me-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{CO}$ , 63625-79-6;  $\text{Fe}(\text{CO})_2(\eta^4\text{-4-Me-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{PPh}_3$ , 63625-81-6;  $\text{Fe}(\text{CO})_2(\eta^4\text{-3-NO}_2\text{-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{CO}$ , 63625-82-7;  $\text{Fe}(\text{CO})_2(\eta^4\text{-2-NO}_2\text{-C}_6\text{H}_4\text{CH}=\text{CHCHO})\text{CO}$ , 63625-83-8;  $\text{Fe}_2(\text{CO})_9$ , 15321-51-4;  $\text{PPh}_3$ , 603-35-0;  $\text{SbPh}_3$ , 603-36-1.

**Supplementary Material Available:** Tables of elemental analyses and melting points of the new compounds and kinetic data at various concentrations and temperatures for the reactions studied (three tables) (4 pages). Ordering information is given on any current masthead page.

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## Isomerization of the Alkyl Group in $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{alkyl})$ Complexes

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The *sec*-butyl group in  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{sec-butyl})$  isomerizes to a *n*-butyl group when heated for 4 h at 63 °C in xylene. Some  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)\text{H}$  is also isolated from this isomerization reaction as well as butenes due to a competitive thermal decomposition reaction. The deuterium label in  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{isobutyl-}i{1,1-d}_2)$  is scrambled when this complex is heated for 2.5 h at 65 °C in xylene solution in reisolated alkyl and in the 2-methylpropene produced from the thermal decomposition reaction. This shows that transition metal to tertiary carbon intermediates are accessible in these isomerization reactions. In addition,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(2\text{-methylbutyl})$  isomerizes to a 5.7 to 1 mixture of the 3-methylbutyl to 2-methylbutyl derivative over a 4-h period at 64 °C demonstrating that the iron has a fairly strong preference for a primary carbon  $\beta$  to a secondary carbon over a primary carbon  $\beta$  to a tertiary carbon.

### Introduction

The preference of transition metals for different types of carbon atoms during a catalytic process such as olefin isomerization or hydroformylation reactions strongly influences the product ratios.<sup>1</sup> Investigations into the criteria for the stability of varying types of metal alkyls are thus important. In a study by Bennett and Charles<sup>2</sup> on the oxidative addition of acyl halides to  $\text{IrCl}(\text{N}_2)(\text{PPh}_3)_2$  which yields the alkyliridium compounds  $\text{Ir}(\text{Cl})_2\text{R}(\text{CO})(\text{PPh}_3)_2$ , it was shown that if the acyl halide is branched at the  $\alpha$ -carbon atom, the resulting alkyliridium complex is exclusively the straight-chain compound. It was proposed that the instability of the *sec*-alkyls was due to steric interactions of the branched alkyls with the phenyl rings of the triphenylphosphine ligands. Kumada and co-workers<sup>3</sup> have reported on the catalytic activity of nickel diphosphine complexes in the cross coupling of Grignard reagents with olefinic and aromatic halides and have shown that the coupling reaction was accompanied by alkyl group isomerizations from secondary to primary carbons. The extent of the isomerization was dependent on the electronic nature of the phosphine ligand of the catalyst. They invoked a mechanism that involved the formation of  $\sigma$ -alkyl intermediates

followed by hydridoolefinnickel intermediates to account for the product distributions received. Kochi has shown that an isopropylgold(III) complex can isomerize to the *n*-propyl derivative.<sup>4</sup> In addition, the alkylzirconium complexes produced from the reaction of  $(\eta^5\text{-C}_5\text{H}_5)_2\text{Zr}(\text{Cl})\text{H}$  with internal olefins rearrange rapidly to the primary alkyls although this isomerization cannot proceed past a tertiary carbon.<sup>5</sup> In a study by Casey et al.<sup>6</sup> on the thermal decomposition of the erythro and threo isomers of (2,3-dimethylpentanoyl)manganese pentacarbonyl, (4-methylhexanoyl)manganese pentacarbonyl, and (3-ethylpentanoyl)manganese pentacarbonyl, it is shown that a tertiary carbon intermediate (a 3-methyl-3-pentylmanganese species) was high in energy and acted "as a roadblock along the alkene isomerization pathway".

Reported in this paper are results for a system,  $(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{PPh}_3)(\text{alkyl})$ , that is well suited for a study of metal-alkyl isomerizations. Using this system, it has been shown that isomerization reactions can readily take place through tertiary carbon atoms and that slight changes in substitution at the carbon  $\beta$  to the metal center also have an important influence on the isomerization if alkyls. We have previously determined the mechanism of thermal decompo-