Journal of Organometallic Chemistry, 160 (1978) 467—475
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THE REACTION OF TRICHLOROSILYLTETRACARBONYLIRON HYDRIDE ($HFe(CO)_4SiCl_3$) WITH CONJUGATED DIENES

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(Received May 26th, 1978)

Summary

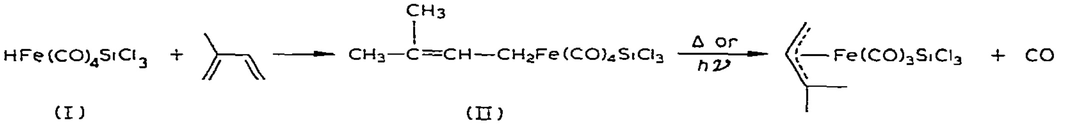
Isoprene, 1,3-butadiene and 2,3-dimethyl-1,3-butadiene react with $HFe(CO)_4SiCl_3$ by addition of the Fe—H function to the diene. Isoprene appears to add predominantly 1,4 and 2,3-dimethyl-1,3-butadiene appears to add 1,2, while 1,3-butadiene may add both ways. In the case of isoprene and 1,3-butadiene loss of CO from the addition compound gives a stable π-allyl-$Fe(CO)_3SiCl_3$ product. Either *cis*- or *trans*-1,3-pentadiene is reduced to pentene by $HFe(CO)_4SiCl_3$.

Introduction

The addition of transition metal hydrides to unsaturated organic compounds has been shown to be a useful route to organotransition metal species. In most cases complexation of the organic substrate by a coordinatively unsaturated transition metal hydride precedes the formation of the metal-to-carbon σ bond [1]. There are a few cases involving conjugated dienes in which very stable transition metal hydrides have been used where the metal hydride addition is probably directly to the unsaturated carbon—carbon bond, without prior loss of ligand by the metal [2]. It appears that in the addition of trichlorosilyltetracarbonyliron(II) hydride(I) [3] to conjugated dienes, reported here, the reaction takes place withour prior loss of carbon monoxide. The nature of the products of this reaction depends on the diene used as is discussed below.

Results

Equation 1 describes the reaction between trichlorosilyltetracarbonyliron(II) hydride and isoprene. Compounds I and II are quite air sensitive. Compound III is moisture sensitive and slowly decomposes in solution but it does not have to be kept rigorously air-free as do I and II.

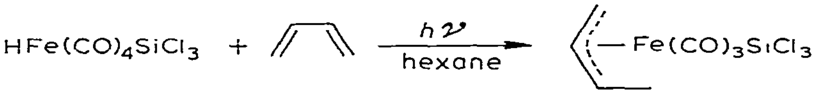


(1

(I) (II) (III)

Compound III has been fully characterized as described below; compound II has not been isolated but its PMR and IR spectra have been observed.

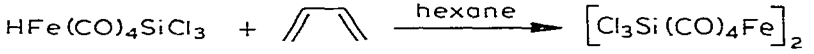
The transformation of II to III occurs slowly in solution at room temperature. However, the product thus obtained is contaminated by an air-sensitive impurity. The photochemical synthesis gives a higher yield of purer material. Equation 2 describes the reaction between compound I and 1,3-butadiene:



(2)

(IV)

In this case the yield of the η^3 product (compound IV) (see the Experimental Section) is much lower than in the case of isoprene. It was not possible to obtain any η^3 product in the absence of photolysis, the only product obtained being the iron—iron dimer (V) as shown in eq. 3. This same product was obtained by Jetz and Graham in the reaction between compound I and tetrafluoroethylene [3].



(3)

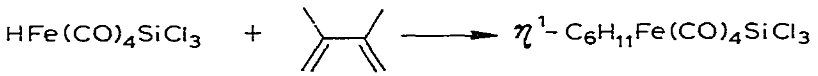
(V)

In the case of 1,3-butadiene the IR spectrum of the η^1 addition product was observed in solution. It was not possible to obtain the PMR spectrum of this material since the reaction mixtures rapidly became heterogeneous.

Both *cis*- and *trans*-1,3-pentadiene react with compound I to produce the iron—iron dimer V. In the case of *trans*-1,3-pentadiene we isolated the hydrocarbon fraction and found that pentene-2 was the only olefin present (eq. 4). No evidence of an organoiron intermediate was found in this reaction.

$$HFe(CO)_4SiCl_3 + C_5H_8 \rightarrow C_5H_{10} + [Cl_3Si(CO)_4Fe]_2 \qquad (4)$$

In the reaction between compound I and 2,3-dimethyl-1,3-butadiene either addition or reduction occurred depending on the relative amount of reactants used. When the ratio of compound I to 2,3-dimethyl-1,3-butadiene was 1 : 10, addition occurred as indicated in eq. 5. Photolysis of the resulting solution did not produce any η^3 product analogous to compound III. We were able to obtain the IR spectrum of compound(s) VI. Attempts to obtain useful PMR spectra

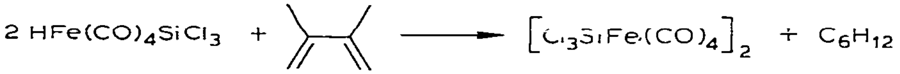


(5)

(VI)

were frustrated by our inability to obtain a solution of VI uncontaminated with starting material and/or products.

When the ratio of I to 2,3-dimethyl-1,3-butadiene was 1 : 1 (or 2 : 1) the reaction proceeded essentially as described in eq. 6. Examination of the hydrocarbon fraction resulting from this reaction showed it to be a mixture of materials containing mostly 2,3-dimethylbutene-1. Some saturated material was also present, as well as some starting material.



(6)

Identification and characterization of products

Table 1 lists elemental analytical data and spectroscopic data for the new η^1- and η^3-alkenyliron compounds described here. The PMR spectrum of compound II shows it to be the 1,4 adduct of isoprene in which the iron is attached to the less branched end of the chain. The 2042 cm^{-1} band in the IR spectrum is broader than the other two carbonyl bands suggesting some degeneracy which prevents us from observing the four carbonyl stretching bands expected for the *cis* isomer [4]. Graham has observed mixtures of *cis* and *trans* isomers with rapid interconversion for similar compounds [5]. The 1638 cm^{-1} band disappears as the $\eta^1 \rightarrow \eta^3$ conversion occurs in solution, suggesting that this is the assigned $\nu(C{=}C)$ for compound II. We were not able to find the similar band for the other η^1 compounds reported here.

The PMR spectrum for compound III is unequivocal and the IR spectrum contains the expected three carbonyl stretching bands [4]. The IR spectrum of compound IV also shows the expected three carbonyl bands. The PMR spectrum of IV indicates that it is the less stable *anti* isomer. The non-zero H_c—H_d coupling suggests the long range found in the "W" configuration [6]. Also J_{de} is in the range expected for *cis* coupling. There is a slow transformation of this material to the *syn* isomer at 37°C in solution. The transformation was incomplete in 2.5 months and is accompanied by decomposition in solution.

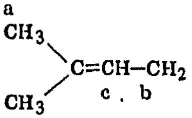
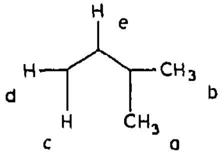
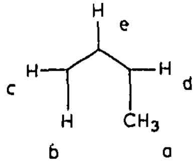
When compound I is mixed with an excess of 1,3-butadiene, isoprene or 2,3-dimethyl-1,3-butadiene, the carbonyl bands due to I rapidly disappear and are replaced by the bands listed in Table 1. The PMR spectrum obtained for compound II allowed us to identify the isomer present. As discussed below, we suspect that there is at least some 1,2 addition in the case of the other dienes, but we have no direct spectroscopic evidence of it.

Discussion

The reaction between compound I and isoprene gives the regiospecific 1,4 adduct II which loses carbon monoxide either thermally or photochemically to give the η^3 species III. There is ample precedent for this type of reaction, both with non-labile transition metal hydrides such as $HMn(CO)_5$ [7] and η-$C_5H_5Fe(CO)_2H$ [8], and with labile transition metal hydrides such as $HCo(CO)_4$ [9] and $HNi[P(OR)_3]_4^+$ [10]. In the case of the non-labile hydrides, the η^1 intermediate was observed and shown to be the 1,4 adduct while in the case of the

TABLE 1

ANALYTICAL AND SPECTROSCOPIC DATA FOR PREVIOUSLY UNREPORTED COMPOUNDS

Compound	PMR [a]		IR [b]		M.p. (°C)	Elemental analysis		
	Signal	Assignment	Band	Assignment		Element	Found	Calcd.
$(CH_3)_2C{=}CHCH_2Fe(CO)_4SiCl_3$ (II)			2110m 2055m 2042s(br)	ν(CO)		Not isolated		
	1.60(6) 2.60(2) 5.50(1)	a, a' b (J_{bc} 8 Hz) c	1638	ν(C=C)				
η^3-$C_5H_9Fe(CO)_3SiCl_3$ (III)			2069m 2019m 2003s	ν(CO)	60	C H Fe Si Cl	27.9 3.1 14.9 8.4 29.5	(27.9) (2.6) (16.2) ((8.1) (30.9)
	0.8(3) 1.47(4) 2.47(1) 4.13(1)	a b, c d, (J_{de} 7 Hz) e (J_{ce} 12 Hz)						
η^1-$C_4H_7Fe(CO)_4SiCl_3$	Data not obtained		2111m 2060m 2042s(br)	ν(CO)		Not isolated		
anti-η^3-$C_4H_7Fe(CO)_3SiCl_3$ (IV)			2075s 2025s 2012s	ν(CO)	63	C H	25.9 2.3	(25.6) (2.3)
	0.8(3) 2.1(1) 2.7(1) 3.9(1) 4.5(1)	a (J_{ad} 6 Hz) b (J_{be} 12 Hz, J_{bc} ~1 Hz) c (J_{ce} 6 Hz, J_{bc}, J_{cd} ~1 Hz) d (J_{de} 8 Hz) e						
η^1-$C_6H_{11}Fe(CO)_4SiCl_3$ (VI)	Data not obtained		2105m 2058m 2037s(br)	ν(CO)		Not isolated		

[a] C_6D_6 solution, δ scale; integral values in parenthesis. [b] Pentane solution.

labile hydrides the η^3 product only was isolated and the details of the mechanism are less clear.

We observed that the rate of the reaction between I and isoprene was the same in the presence (one atmosphere) and absence of carbon monoxide. This suggests that the reaction is a direct metal hydride addition, not preceded by loss of CO. This is in contrast to the addition of $HFe(CO)_4^-$ to α,β-unsaturated carbonyl compounds which is greatly inhibited by the presence of carbon monoxide (11). We have no evidence to decide whether the addition is due to the large acid strength of I or whether it is a free radical reaction.

In the reaction between compound I and 1,3-butadiene the best product yield obtained in several reactions was 20%. Two possible explanations for the low yield are (i) the competition of 1,2 vs. 1,4 addition or (ii) the reaction described in eq. 7. While the reaction shown in eq. 7 does occur (vide infra), we

$$\eta^1C_4H_7Fe(CO)_4SiCl_3 + \mathrm{I} \rightarrow C_4H_8 + \mathrm{V} \tag{7}$$

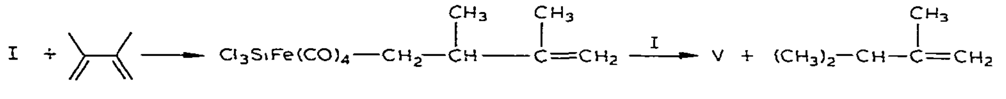
were not able to increase our yield by completely converting compound I to the η^1 species prior to initiating the photolysis. Also, removal of compound IV and the volatile constituents of the product mixture yielded a viscous residue which had a very complex carbonyl (IR) spectrum and an absorption at 1645 cm^{-1}, characteristic of a terminal olefin.

Of course, homolytic cleavage of the iron—carbon bond in the η^1 species would account for the formation of V rather than IV, but that reaction appears to be rather slow at least for the other η^1 species obtained.

From the work of Collman it is known that iron—carbon σ bonds in compounds of the type $RFe(CO)_4^-$ are readily cleaved by acid [12]. The reaction shown in eq. 7 may be considered to be such an acid cleavage since it has been shown that compound I is a very strong acid [13].

The isomer of η^3-$C_4H_7Fe(CO)_3SiCl_3$ formed from compound I and 1,3-butadiene is the less stable *anti* isomer. This suggests that compound I reacts initially with the *s-cis* rotamer of 1,3-butadiene. Such selectivity has been reported with $NHi[P(OR)_3]_4^+$ [10] and in a photochemical system involving $Cr(CO)_6$ [14]. In our case the *anti* isomer slowly converts into the *syn* isomer in solution. We were unable to study the conversion quantitatively due to the thermal instability of the species in solution. Nesmeyanov and coworkers reported that η^3-$C_3H_5Fe(CO)_3X$ (X = halogen) is unstable in solution at room temperature [15]. Graham and coworkers have reported the synthesis of η^3-$C_3H_5Fe(CO)_3SiCl_3$, but there is no information about its stability in solution [16].

The IR spectrum of the solution indicates that compound I is rapidly and completely converted to the η^1 species when it is treated with a 10 : 1 excess of 2,3-dimethyl-1,3-butadiene. Photolysis of this solution yielded, on workup, a viscous residue from which we were not able to isolate a pure compound. When the diene/iron hydride ratio was reduced to 2 : 1, compound V was produced, suggesting reduction of the diene. Therefore an experiment was carried out in



$$\mathrm{I} + \longrightarrow Cl_3SiFe(CO)_4{-}CH_2{-}\overset{\displaystyle CH_3}{\overset{|}{C}H}{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 \xrightarrow{\mathrm{I}} \mathrm{V} + (CH_3)_2{-}CH{-}\overset{\displaystyle CH_3}{\overset{|}{C}}{=}CH_2 \tag{8}$$

which the diene/iron hydride ratio was 1 : 2. The hydrocarbon product obtained consisted of mainly 2,3-dimethylbutene-1. This suggests that the reaction can be described by eq. 8. The second step apparently occurs slightly faster than the first step since a considerable excess of the diene is necessary to cause the reaction to stop at addition. Also, apparently there is some reduction of the olefin product since there was diene left even in the case where the stoichiometric amount of iron hydride was used. It has been reported that pentacarbonylmanganese hydride reduces 2,3-dimethyl-1,3-butadiene rather than producing the η^3-allylic manganese tetracarbonyl [6].

The reaction between compound I and 1,3-pentadiene can be explained in terms of an initial 1,2 addition followed by a very fast second step in which a second mole of compound I reacts with the η^1 intermediate, giving the observed products. It is not clear why the second step should be relatively so much faster here than it is in the case of the other dienes investigated. Labile transition metal hydrides will react with 1,3-pentadiene to give η^3 adducts [9] but the reaction of other non-labile transition metal hydrides with 1,3-pentadiene has not been reported.

Experimental

General

Infrared spectra were obtained using a Perkin—Elmer model 621 or a Beckman model 8 spectrophotometer. Nuclear magnetic resonance spectra were obtained using a Hitachi Perkin—Elmer model RB24 or a Varian T-60 spectrometer. Elemental analyses were performed by the Schwarzkopf Micro-Analytical Laboratory, Woodside, NY.

Trichlorosilane was obtained from Petrarch Systems Inc., Levitown, PA, and used as received. Iron pentacarbonyl was obtained from Alfa Products, Danvers, MA, and used as received. Butadiene-1,3 was obtained from Air Products, Inc., Kansas City, MO and used as received, the other dienes and 2,3-dimethylbutene-1 were obtained from Chemical Samples Inc., Columbus, OH. They were vacuum distilled from calcium hydride immediately before use. All operations involving compound I and the η^1 species reported here were either carried out in a high vacuum system or under dry, oxygen-free nitrogen.

Compound I was prepared as reported [3]. It was usually vacuum distilled prior to use.

Preparation of η^3-$C_5H_9Fe(CO)_3SiCl_3$: The reaction vessel used here was a vacuum sublimator of 300 ml capacity. The reactor was flushed with nitrogen and charged with a solution containing 3 g of compound I and 100 ml of petroleum ether. Subsequently, 20 ml of isoprene was added. The reaction mixture was kept cool by circulation of a coolant through the cold finger. The IR spectrum of the reaction mixture was checked periodically until the conversion to compound II was complete. The reaction vessel then was transferred to a Rayonet Photochemical Reactor fitted with 3500 Å lamps. Overnight photolysis of the reaction mixture yielded a cloudy solution which was filtered in air.

The clear filtrate was cooled to −78° and the product, a bright yellow solid, came out of solution. It was isolated by decanting the supernatant liquid and then pumping off the last traces of solvent. Due to its moisture sensitivity, the product was transferred to the weighing vessel in an I^{2}R glove bag under a nitrogen atmosphere. The yield of material obtained in this way was 1.6 g (48%).

Using butadiene as a starting material, the above technique resulted in isolated yields of 9, 13 and 20% on different occasions.

When 2,3-dimethyl-1,3-butadiene was used as the starting diene, the IR spectrum of the solution indicated that η^1-$C_6H_{11}Fe(CO)_4SiCl_3$ had formed. However, on cooling of the photolyzed reaction mixture nothing came out of solution. Removing the volatile material under vacuum resulted in a viscous material which exhibited broad NMR signals in solution.

When compound I and 1,3-pentadiene (*cis* or *trans*) were mixed in the presence or absence of solvent, the IR spectrum indicated the formation of compound V.

Compound V was identified by its mass spectrum which showed a weak parent ion peak and a very strong $Fe(CO)_4SiCl_3^+$ peak along with the expected fragmentation patterns for these two ions. The IR spectrum of the material thus identified, which was similar to that previously reported [3], was used as a standard which allowed us to detect compound V in solution.

Reaction between I and η^1-$C_4H_7Fe(CO)_4SiCl_3$: Two 30 ml erlenmeyer flasks containing 20 ml hexane each were capped with serum stoppers and flushed with nitrogen. Each solution then was saturated with 1,3-butadiene and 1 ml I was added to each with a syringe. The IR spectrum of each solution showed that I had been converted to η^1-$C_4H_7Fe(CO)_4SiCl_3$, i.e. the 2126 cm^{-1} band of I had disappeared and was replaced by a band at 2110 cm^{-1}. The butadiene then was removed from each solution by pumping on it through a syringe needle. The IR spectra of the two solutions were checked again at this point.

Approximately 1 ml of I was added to one of these solutions (referred to as solution A below) and the IR spectrum of each was observed periodically. Within 18 h all the IR bands in the 2000—2150 cm^{-1} range of solution A could be accounted for by compound V while the control solution still exhibited a strong band at 2110 cm^{-1}, indicating the continued presence of η^1-C_4H_7Fe-$(CO)_4SiCl_3$.

The IR spectrum of compound II was obtained as follows: A 0.05 *M* solution of compound I in cyclopentane was diluted to 0.01 *M* with a solution of isoprene in cyclopentane sufficient to provide at least a 10 : 1 excess of isoprene. The solution thus obtained was injected into a 0.1 mm KBr solution cell. Within 30 min the carbonyl bands due to compound I had disappeared, being replaced by those of compound II. Observation of the 1638 cm^{-1} band was made on the 0.05 *M* solution of I containing approximately an equimolar amount of isoprene.

Similar experiments were carried out with 1,3-butadiene and 2,3-dimethyl-1,3-butadiene to observe the spectra reported for the other η^1 compounds reported here.

Observation of the NMR spectrum of compound II was done as follows: A solution of compound I in C_6D_6 was filtered into an NMR tube using high vacuum techniques. An excess of isoprene then was distilled in and the reagents were mixed by shaking the apparatus containing the NMR tube. After about 10 min, the NMR tube was pumped on until half the volatiles had been pumped away. The NMR tube was then sealed. The NMR spectrum obtained immediately thereafter was that of compound II. 72 h later the NMR spectrum of this solution was that of compound III.

Reaction between I and isoprene in the presence and absence of CO: The final concentrations of the solutions made up here were such that the carbonyl bands stayed on scale and there was a large excess of isoprene present. Ten ml of a stock solution of compound I in hexane was put in each of two 30 ml erlenmeyer flasks capped with serum stoppers. One container was flushed with nitrogen and the other with CO. Into one container 0.4 ml of isoprene was injected and after shaking a sample was taken and injected into an IR cell. The IR spectrum was observed periodically with attention paid to the 2126/2110 cm^{-1} band ratio. The half-time of the reaction was taken to be the time at which these two bands had equal heights.

After the first experiment was finished, 0.4 ml of butadiene was injected into the other solution and the half-time of that reaction obtained. Within experimental error, both half times were 5 min under these conditions.

Stoichiometric reactions of I: To 4.7 g of I (16 mmol) in 18 ml of dodecane, placed in a Schlenk tube in a nitrogen atmosphere, was added 0.6 g (7.3 mmol) of 2,3-dimethyl-1,3-butadiene. The reaction initially was exothermic and the mixture was stirred for 2 h after which the volatile material was distilled into a collection vessel under vacuum. On a 1/8" × 5' GC colums packed with Apiezon L on Chromosorb the product mixture thus obtained shows six peaks. One of them accounted for about 70% of the total and had an identical retention time to that of authentic 2,3-dimethylbutene-1.

The NMR spectrum of the material thus obtained is dominated by a doublet ($J = 6$ Hz) at δ 1.08 ppm, a singlet of δ 1.68 ppm and a broad singlet at δ 4.75 ppm, all of which are characteristic of 2,3-dimethylbutene-1.

In a seperate experiment, compound I was added to a large excess of pure *trans*-1,3-pentadiene and all the volatile material was removed after a few hours. The gas chromatogram of this product mixture showed it to be a mixture of pentene-2 (geometrical isomers not resolved) and starting material.

Acknowledgement

We thank the UMKC School of Graduate Studies for financial support of this work.

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