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IRON CARBONYL π-COMPLEXES OF VINYLSILANES, VINYLDISILANES AND VINYLSILOXANES

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Summary

It is shown that iron carbonyls react with vinylsilanes, $CH_2{=}CHSiR_3$ (where R is Me, OMe, $CH{=}CH_2$ or Cl) and vinylsiloxanes to give rise to iron tetracarbonyl π-complexes. If two or more vinyl groups are attached to the silicon atom, iron tricarbonyl compounds similar to 1,4-diene complexes are also formed. The reaction of 1,2-divinyltetramethyldisilane with $Fe_2(CO)_9$ unexpectedly leads also to mono- and bis(iron tetracarbonyl) complexes. IR, ^1H and ^{13}C NMR, and mass spectra of the compounds obtained are discussed and some chemical conversions are performed.

Introduction

There is a vast body of information concerning olefin π-complexes with transition metals [1]. The π-complexes of vinylsilanes have received much less attention. The few investigations on this subject have dealt with some tricarbonyl complexes of Fe, Mo and W with divinyldimethylsilane [2,3], tetracarbonyl complexes of Mo and W with tetravinylsilane [4], Cu^I [5], Pt^0 and Pt^{II} [6,7] complexes with monovinylsilanes.

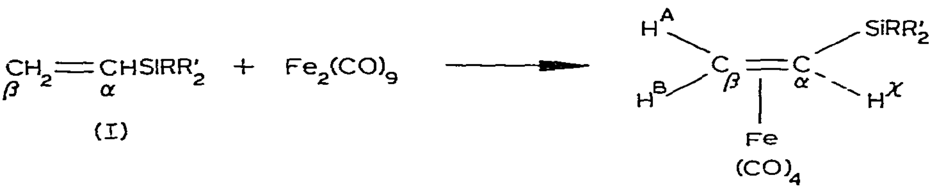
Comparison shows that during oligomerisation [8], polymerisation [9] and telomerisation [10] with the use of organometallic catalysts vinylsilanes behave as α-olefins. At the same time α-olefins containing no acceptor substituents at the double bond are known to form unstable π-complexes [11]. Therefore, it appeared of interest to investigate whether π-olefin complexes would result from the reaction between vinylsilanes and iron carbonyls.

As evidenced by photoelectron spectra and ^{13}C NMR, the introduction of a silyl group changes the physico-chemical characteristics of a double bond [12]. The trimethoxysilyl group in vinyltrimethoxysilane, for instance, decreases the electron density of the double bond, so that the first ionisation potential of its π-electrons increases from 9.5—9.7 eV (for α-olefins) to 11 eV [13]. This suggests that vinylsilanes would give more stable π-complexes than do α-olefins.

The synthesis of iron tetracarbonyl π-complexes with several vinylsilanes was described recently in our brief reports [14,15]. The present paper is concerned with a detailed investigation of these complexes, as well as the products of the reaction between 1,2-divinyltetramethyldisilane and diiron nonacarbonyl. Also reported are certain newly obtained iron carbonyl π-complexes of vinylsiloxanes.

Results and discussion

To study the complexing ability of the vinylsilanes (I) with diiron nonacarbonyl, vinyltrimethyl-, vinyltrimethoxy-, divinyldimethyl- and tetravinylsilane were chosen. All these compounds in the presence of an equimolar amount of $Fe_2(CO)_9$ in heptane solution gave rise after 2—3 hours at 35—40°C to relatively stable iron tetracarbonyl π-complexes (II—V).



(II, R = R' = Me;
III, R = R' = OMe;
IV, R = CH=CH$_2$, R' = Me;
V, R = R' = CH=CH$_2$)

Several months storage at 0°C under an inert gas did not alter the properties of these compounds. Their solutions in organic solvents are less stable. For example, ^{1}H NMR evidence was obtained that after nine days of being kept at room temperature in sealed tubes, deuteroacetone solutions of complexes II and III contained uncoordinated vinylsilanes (45 and 15%, respectively).

The physical characteristics of the π-complexes are given in Tables 1, 2 and 3. One can see that the IR spectra of II—V in heptane solution in the 2090—1980 cm^{-1} region closely resemble those typical of π-iron tetracarbonyl olefin derivatives [14]. The presence of four CO bands in the IR spectra indicates that one equatorial CO group in the trigonal-bipyramidal $Fe(CO)_5$ molecule underwent substitution by vinylsilane. The stretching band of the coordinated olefin bond was shifted towards the long-wave region by more than 100 cm^{-1} (Table 2).

In comparison with the free ligand, the ^{1}H NMR spectra of the complexes, as is the case with carbon analogues [16], show a characteristic upfield shift of olefin protons. For example, the olefin protons resonate at 2.3—3.2 ppm in complex II and at 5.5—6.5 ppm in the original silane. In the ^{13}C NMR spectra of the original vinylsilanes the signal of the atoms C_α and C_β resonate at 130—

(continued on p. 378)

TABLE 1

ANALYTICAL DATA

Compound	Yield (%)	m.p. (°C)	Formula	Analysis Found (calcd.) (%)			
				C	H	Cl	Fe
$(CH_2{=}CHSiMe_3)Fe(CO)_4$ (II)	39		$C_9H_{12}FeO_4Si$	40.44 (40.13)	4.57 (4.51)	—	19.51 (20.83)
$[CH_2{=}CHSi(OMe)_3]Fe(CO)_4$ (III)	55		$C_9H_{12}FeO_7Si$	34.16 (34.20)	3.74 (3.83)	—	17.15 (17.09)
$[(CH_2{=}CH)_2SiMe_2]Fe(CO)_4$ (IV)	28		$C_{10}H_{12}FeO_4Si$	42.65 (42.87)	4.32 (4.32)	—	20.18 (19.94)
$[(CH_2{=}CH)_4Si]Fe(CO)_4$ (V)	31		$C_{12}H_{12}FeO_4Si$	47.56 (47.39)	3.96 (3.98)	—	16.93 (18.36)
$[(CH_2{=}CH)_4Si][Fe(CO)_3]_2$ (VI)	45	73	$C_{14}H_{12}Fe_2O_6Si$	40.36 (40.42)	2.93 (2.91)	—	26.02 (26.85)
$(CH_2{=}CHSiMe_2Cl)Fe(CO)_4$ (IX)	47		$C_8H_9ClFeO_4Si$	34.17 (33.30)	3.26 (3.14)	12.18 (12.29)	18.70 (19.36)
$(CH_2{=}CHSiMe_2OH)Fe(CO)_4$ (X)	50	44	$C_8H_{10}FeO_5Si$	35.60 (35.57)	3.76 (3.73)	—	20.87 (20.68)
$[(CH_2{=}CHSiMe_2)_2O][Fe(CO)_4]_2$ (XI)	20		$C_{12}H_{18}Fe_2O_9Si_2$	37.50 (36.80)	3.53 (3.48)	—	20.54 (21.39)
$[(CH_2{=}CHSiMe_2)_2]Fe(CO)_4$ (XII)	17		$C_{12}H_{18}FeO_4Si_2$	42.65 (42.61)	5.21 (5.36)	—	15.59 (16.51)
$[(CH_2{=}CHSiMe_2)_2][Fe(CO)_4]_2$ (XIII)	17	52—53	$C_{16}H_{18}Fe_2O_8Si_2$	38.20 (37.97)	3.65 (3.58)	—	21.18 (22.07)
$[(CH_2{=}CHSiMe_2)_2O]Fe(CO)_4$ (XV)	17		$C_{16}H_{18}FeO_5Si_2$	40.97 (40.68)	5.22 (5.12)	—	—
$[(CH_2{=}CHSiPh_2)_2O]Fe(CO)_4$ (XVI)	10		$C_{32}H_{26}FeO_5Si_2$	63.97 (63.81)	4.37 (4.32)	—	9.30 (9.27)
$[(CH_2{=}CHSiPh_2)_2O]Fe(CO)_3$ (XVIII)	11	65 (decomp.)	$C_{31}H_{26}FeO_4Si_2$	65.12 (64.83)	4.71 (4.53)	—	9.89 (9.72)
$[(CH_2{=}CHSiMeO)_4]Fe(CO)_4$ (XIX)	41		$C_{16}H_{24}FeO_8Si_4$	38.52 (37.50)	4.72 (4.72)	—	10.26 (10.90)

TABLE 2

IR, ^{1}H NMR AND MASS SPECTRA

Compound	ν (cm^{-1})			δ (ppm) [a]				
	C≡O (heptane)	C=C		Free ligand	Complex			
		Free ligand	Complex		H_A	H_B	H_X	Others
II	2083, 2011, 2003, 1984	1596	1470	0.07 (CH_3) 5.54—6.45 ($CH=CH_2$)	2.69	3.16	2.29	0.14 (CH_3
III	2090, 2019, 2011, 1987	1602	1470	3.71 (OCH_3) 6.05—6.47 ($CH=CH_2$)	2.64	3.12	1.74	3.62 (OCH
IV	2084, 2013(sh), 2004, 1985	1600	1475	0.14 (CH_3) 5.55—6.60 ($CH=CH_2$)	2.69	3.18	2.22	0.24 (CH_3 5.5—6.5 ($CH=CH_2$
V	2085, 2013(sh), 2006, 1987	1592	1472	5.5—6.4 ($CH=CH_2$)	2.71	3.22	2.22	5.5—6.4 ($CH=CH_2$
VI	2048, 2037, 1984, 1970	1592		5.5—6.4 ($CH=CH_2$)		0.85—3.15		—
IX	2087, 2006(br), 1987	1598	1475	0.49 (CH_3) 5.92—6.14 ($CH=CH_2$)	2.71	3.09	2.20	0.22 (CH 0.29 (CH
X	2087, 2017(sh), 2008, 1985		1450		2.40	2.71	1.85	0.16 (CH 2.45 (OH
XI	2087, 2008(br), 1986	1605	1425	0.18 (CH_3) 5.64—6.00 ($CH=CH_2$)	2.40	2.73	1.98	0.16 (CH 0.23 (CH
XII	2084, 2010(sh), 2005, 1985	1600	1480 1600	0.13 (CH_3) 5.45—6.4 ($CH=CH_2$)	2.42	2.92	2.05	0.07 (CH 0.28 (CH
XV	2085, 2009(br), 1985	1605	1425	0.18 (CH_3) 5.64—6.00 ($CH=CH_2$)	2.42	2.76	1.98	0.22 (CH 0.26 (CH 0.29 (CH 5.78—6.2 (CH=CH
XVI	2087, 2018, 2010, 1987	1605	1440 [b] 1605	5.51—6.75 ($CH=CH_2$) 7.21—7.78 (C_6H_5)	2.75	3.00	2.2	5.40—6.4 (CH=CH 6.98—7.6 (C_6H_5)
XVIII	2065, 1991(br)	1605	1440 [b]	5.51—6.75 ($CH=CH_2$) 7.21—7.78 (C_6H_5)	2.87—3.42			7.09—8.2 (C_6H_5)
XIX	2089, 2015(sh), 2011, 1987	1615	1420	0.14 (CH_3) 6.00 ($CH=CH_2$)	2.62	2.91	1.93	0.13 (CH 0.31 (CH 5.96 (CH

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[a] ^{1}H NMR spectra of II—V were taken in $(CD_3)CO$; VI, IX—XIII, XV in C_6D_6; XVI, XVIII and XIX in CS_2.

Hz)			Mass spectra (m/e)
	BX	AB	
.5	11.0	1.0	$268[M]^+$; $240[M - \mathrm{CO}]^+$; $212[M - 2\ \mathrm{CO}]^+$; $184[M - 3\ \mathrm{CO}]^+$ $156[M - 4\ \mathrm{CO}]^+$; $100[M - 4\ \mathrm{CO} - \mathrm{Fe}]^+$
5	11.0	0.5	$288[M - \mathrm{CO}]^+$; $260[M - 2\ \mathrm{CO}]^+$; $232[M - 3\ \mathrm{CO}]^+$; $204[M - 4\ \mathrm{CO}]^+$;
.0	11.0	—	$252[M - \mathrm{CO}]^+$; $224[M - 2\ \mathrm{CO}]^+$; $196[M - 3\ \mathrm{CO}]^+$; $168[M - 4\ \mathrm{CO}]^+$; $112[M - 4\ \mathrm{CO} - \mathrm{Fe}]^+$
.0	11.5	1.0	$276[M - \mathrm{CO}]^+$; $248[M - 2\ \mathrm{CO}]^+$; $220[M - 3\ \mathrm{CO}]^+$; $192[M - 4\ \mathrm{CO}]^+$; $136[M - 4\ \mathrm{CO} - \mathrm{Fe}]^+$
	—	—	$388[M - \mathrm{CO}]^+$; $360[M - 2\ \mathrm{CO}]^+$; $332[M - 3\ \mathrm{CO}]^+$; $304[M - 4\ \mathrm{CO}]^+$; $276[M - 5\ \mathrm{CO}]^+$; $248[M - 6\ \mathrm{CO}]^+$; $192[M - 6\ \mathrm{CO} - \mathrm{Fe}]^+$; $136[M - 6\ \mathrm{CO} - 2\ \mathrm{Fe}]^+$
.5	13.5	—	$260[M - \mathrm{CO}]^+$; $232[M - 2\ \mathrm{CO}]^+$; $204[M - 3\ \mathrm{CO}]^+$; $176[M - 4\ \mathrm{CO}]^+$; $120[M - 4\ \mathrm{CO} - \mathrm{Fe}]^+$
5	11.5	—	$242[M - \mathrm{CO}]^+$; $214[M - 2\ \mathrm{CO}]^+$; $186[M - 3\ \mathrm{CO}]^+$; $158[M - 4\ \mathrm{CO}]^+$; $102[M - 4\ \mathrm{CO} - \mathrm{Fe}]^+$
.5	10.5	—	$438[M - 3\ \mathrm{CO}]^+$; $410[M - 4\ \mathrm{CO}]^+$; $382[M - 5\ \mathrm{CO}]^+$; $354[M - 6\ \mathrm{CO}]^+$; $326[M - 7\ \mathrm{CO}]^+$; $298[M - 8\ \mathrm{CO}]^+$; $242[M - 8\ \mathrm{CO} - \mathrm{Fe}]^+$
5	9.5	1.5	$422[M - 3\ \mathrm{CO}]^+$; $394[M - 4\ \mathrm{CO}]$; $366[M - 5\ \mathrm{CO}]^+$; $338[M - 6\ \mathrm{CO}]^+$; $310[M - 7\ \mathrm{CO}]^+$; $282[M - 8\ \mathrm{CO}]^+$ $226[M - 8\ \mathrm{CO} - \mathrm{Fe}]^+$; $170[M - 8\ \mathrm{CO} - 2\ \mathrm{Fe}]^+$;
0	11.0	—	$298[M - 2\ \mathrm{CO}]^+$; $270[M - 3\ \mathrm{CO}]^+$; $242[M - 4\ \mathrm{CO}]^+$; $186[M - 4\ \mathrm{CO} - \mathrm{Fe}]^+$
5	10.5	—	
	—	—	
	10.5	1.0	

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act assignment of ν(C=C) in complexes XVI and XVIII is difficult, since Si—C_6H_5 groups absorb in the same area.

TABLE 3

^{13}C NMR DATA (δ, ppm)

Compound	C_α	C_β	CH_3	CO
$(CH_2{=}CHSiMe_3)Fe(CO)_4$ (II)	45.50	41.49	0.45	211.3
$CH_2{=}CHSiMe_3$	139.5	130.6	—1.33	
$[CH_2{=}CHSi(OMe)_3]Fe(CO)_4$ (III)	31.70	38.86	50.15 [a]	210.0
$CH_2{=}CHSi(OMe)_3$	127.7	135.6	49.28 [a]	
$[(CH_2{=}CH)_4Si]Fe(CO)_4$ (V) [b]	38.45	41.17	—	211.0
$(CH_2{=}CH)_4Si$	134.5	135.5	—	—
$[(CH_2{=}CH)_4Si][Fe(CO)_3]_2$ (VI)	55.07 37.79	58.31 47.94	—	211.1
$(CH_2{=}CHSiMe_2OH)Fe(CO)_4$ (X)	43.36	40.06	1.8; 1.3	210.9
$[(CH_2{=}CHSiMe_2)_2][Fe(CO)_4]_2$ (XIII)	43.36	40.83	—1.17; —4.54	211.4; 205.4
$(CH_2{=}CHSiMe_2)_2$	137.6	130.3	—4.73	

[a] OCH_3. [b] Uncoordinated C_α 134.4 ppm, C_β 135.1 ppm.

140 ppm [12], while the signals of the same atoms in the π-complexes are shifted upfield by 89—96 ppm (Table 3). A similar picture was observed in the ^{13}C NMR spectra of olefin π-complexes [17]. The signals of carbon atoms taking no part in π-complex formation remain virtually unchanged.

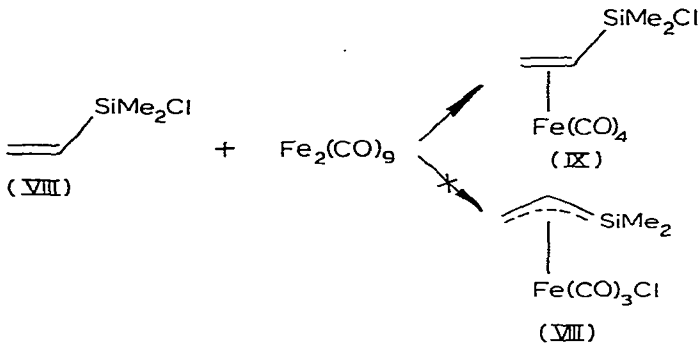
In mass spectral studies only complex II was found to form a molecular ion. The maximum mass number peak in the spectra of complexes III—V correspond to the $[M - CO]^+$ fragment ion. Further fragmentation, which involves consecutive release of CO groups (Table 2) is typical of olefiniron tetracarbonyl complexes.

Along with iron tetracarbonyl compounds IV and V, resulting from the reaction of divinyldimethyl- or tetravinylsilanes with $Fe_2(CO)_9$, minor amounts of tricarbonyl complexes were also formed. Thus, divinyldimethylsilane gave $[(CH_2{=}CH)_2SiMe_2]Fe(CO)_3$ as reported [2]. Tetravinylsilane with $Fe_2(CO)_9$ was found to yield, apart from V, a bis(iron tricarbonyl) complex, $[(CH_2{=}CH)_4Si][Fe(CO)_3]_2$ (VI). This compound was the sole product of UV irradiation of a cyclohexane solution of the iron tetracarbonyl complex V in the presence of $Fe(CO)_5$. The yield of the complex under these conditions was 45%.

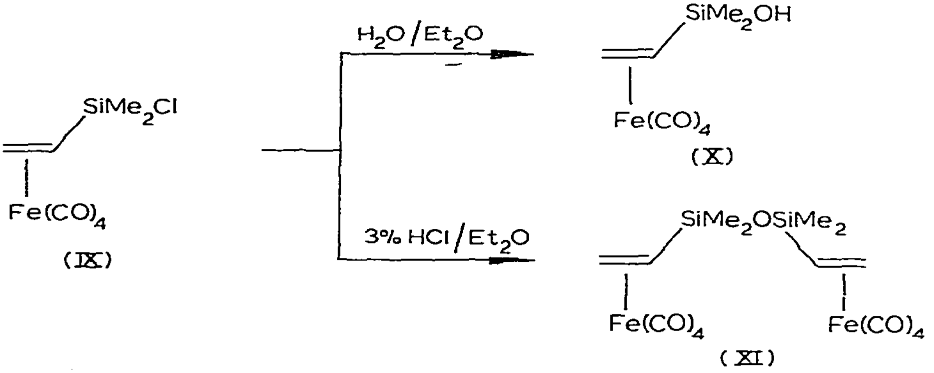
The IR spectrum of VI in cyclohexane contains four stretching frequencies of CO groups in the 2048—1970 cm^{-1} range. In the ^{1}H NMR spectrum of VI the multiplet signal of the vinyl protons is situated at 0.85—3.15 ppm. The ^{13}C NMR spectrum (Table 3) shows four signals of vinyl carbon atoms, which evidently testifies to a pairwise magnetic equivalence of the double bond carbons with respect to the two iron atoms. The structure of (VI) has been determined by an X-ray analysis [18].

Of particular interest was the interaction between vinyldimethylchlorosilane (VII) and $Fe_2(CO)_9$. It seemed likely that the product would be (η^3-1,1-dimethyl-1-silapropenyl)iron tricarbonyl chloride (VIII), since the allyl halides, hydrocarbon analogues of VII, with $Fe_2(CO)_9$ give η^3-allyl complexes [19].

The reaction, however, proved to lead to a usual iron tetracarbonyl π-complex (IX) rather than the π-allyl complex VIII. This was seen in the similarity between the spectral characteristics of IX with those of II—V (Table 2). The formation



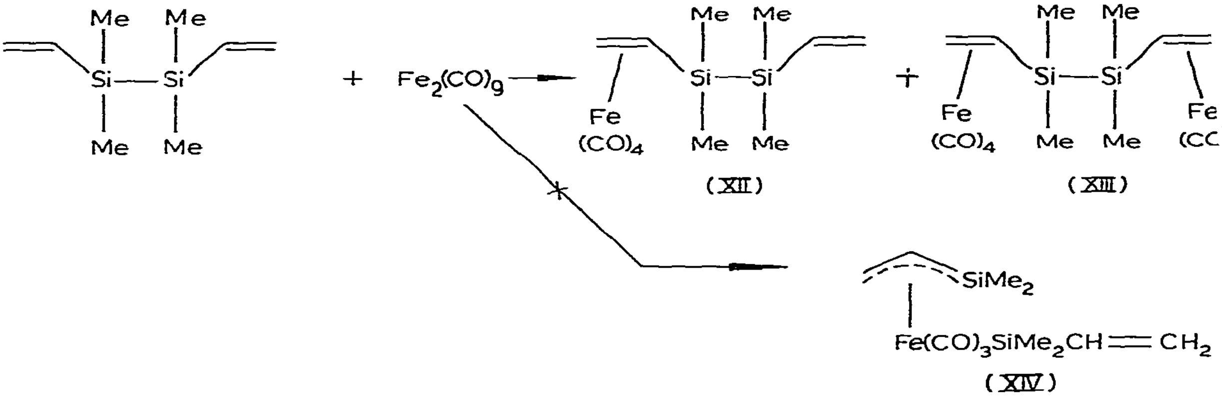
of complex IX with the π-olefin structure was confirmed by its conversion into a silanol (X) and a siloxane (XI) complexes.



Hydrolysis of IX in a water/ether mixture led to (η^2-vinyldimethylsilanol)iron tetracarbonyl (X), a solid substance with m.p. 44°C. The IR spectrum of X in heptane contains four stretching frequencies of CO groups in the 2087—1985 cm^{-1} range and shows a characteristic shift of the C=C band into the longwave region of 180 cm^{-1}. In the 3300 cm^{-1} region there is a broad stretching band of the OH group. In the ^1H NMR spectrum of X vinyl proton signals are displaced upfield to 2.7—1.9 ppm. Hydrolysis of IX by 3% HCl in ether resulted in the bis(tetracarbonylvinyliron)disiloxane complex (XI). As is seen from the spectral data (Table 2), XI is a typical π-olefin complex. The hydrolysis experiments therefore showed that complex IX retains the Si—Cl bond.

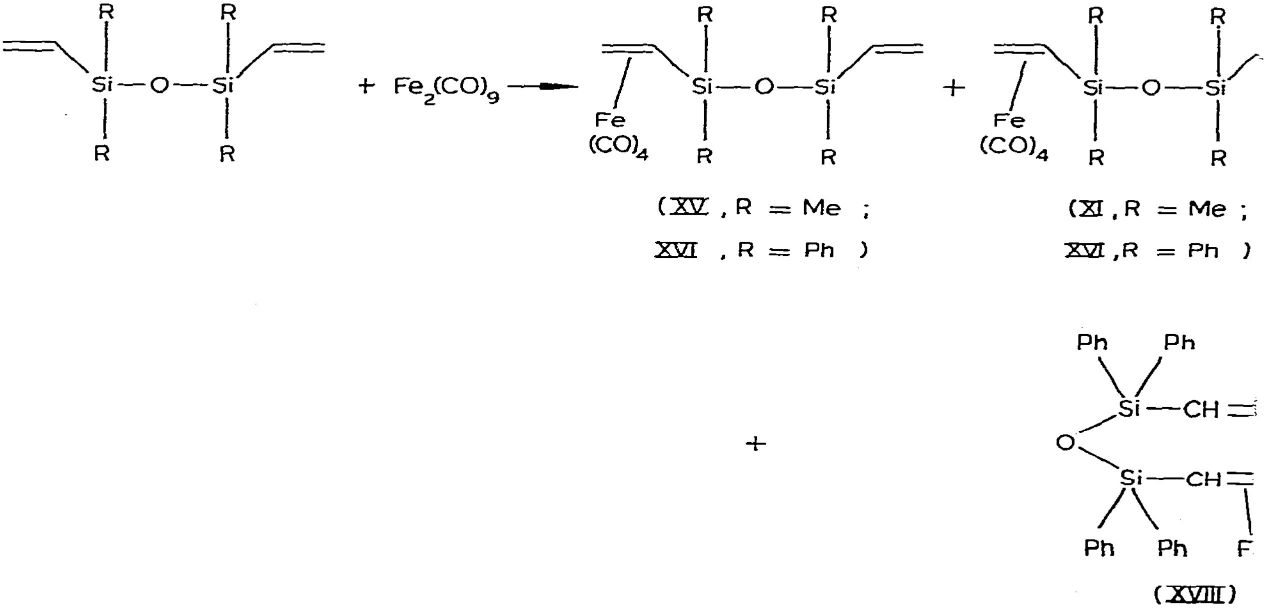
Further attempts to convert (η^2-vinyldimethylchlorosilane)iron tetracarbonyl (IX) into the η^3-silapropenyl complex (VIII) by various reagents or photochemically were unsuccessful. Then we tried to reproduce the synthesis of η^3-silapropenyl complex from 1,2-divinyltetramethylsilane and $Fe_2(CO)_9$ reported in a Japanese study [20]. Surprisingly, the experiment led to no other product but the usual iron tetracarbonyl complexes XII and XIII [15].

The spectral characteristics of XII were similar to those of the complex previously identified [20] as possessing a η^3-silapropenyl structure (XIV). The structure of iron tetracarbonyl π-complexes XII and XIII was confirmed by IR, ^1H NMR and mass spectra and also by ^{13}C NMR data for compound XIII (Table 3). It seems plausible that XII was thought to be an iron tricarbonyl complex [20] because the Japanese workers did not notice (or did not find) the weak band at



2084 cm^{-1} in the IR spectrum. Mass spectral data probably complicates the situation even more, since with vinylsilane iron tetracarbonyl complexes the $[M-\mathrm{CO}]^+$ ion fragment is very often observed rather than the molecular ion (Table 2). Therefore, the conclusion that the reaction product of 1,2-divinyltetramethyldisilane and $Fe_2(CO)_9$ has a η^3-silapropenyl structure appears to be mistaken. The same observation has recently been reported by American authors who studied the reaction between $Fe_2(CO)_9$ and vinylpentamethyldisilane [21].

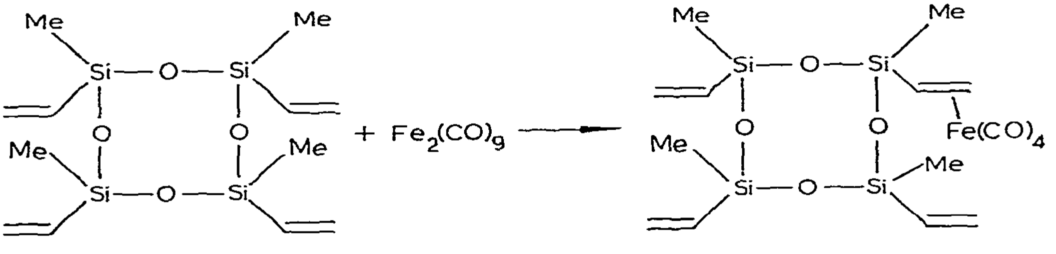
The formation of the bis(iron tetracarbonyl)vinyldisiloxane complex XI in the acid hydrolysis of IX pointed to the feasibility of a direct synthesis of vinylsiloxane complexes with iron carbonyls. Indeed, the reaction of 1,3-divinyltetramethyl- and 1,3-divinyltetraphenyldisiloxanes with $Fe_2(CO)_9$ led to mono- (XV and XVI) and bis(iron tetracarbonyl) (XI and XVIII) complexes, isolated by repeated preparative thin-layer chromatography (TLC).



Also isolated in the reaction with 1,3-divinyltetraphenyldisiloxane was an iron tricarbonyl complex (XVIII), a crystalline yellow substance decomposing above 65°C. As is seen from Table 2, XVIII possesses the same spectral characteristics as the complex VI.

The complexation with iron carbonyls was also extended to polyvinylsiloxane. In an attempt to introduce as many iron tetracarbonyl groups as possible into $[(Me_3SiO_{0.5})_{0.5}(Me_2SiO)_{0.6}(CH_2{=}CHSiMeO)_{0.4}]_{10-12}$ a polysiloxane was produced in which almost all the vinyl substituents were complexed (the product contained 11.8% iron, while the highest theoretically possible amount is ~12%).

Apart from linear siloxanes, cyclic tetravinyltetramethyltetrasiloxane was also used in a reaction with $Fe_2(CO)_9$. After 2 hours at 35—40°C, an equimolar mixture of the reagents in hexane gave rise to a monoiron tetracarbonyl complex (XIX). The integrated ^1H NMR spectrum indicated that only one of the four vinyl groups of the cyclic siloxane is involved in complexation in XIX. This complex may be used for the introduction of a specific number of iron tetracarbonyl groups into a polysiloxane molecule.



(XIX)

Experimental

All the stages of synthesis and isolation of silicone-containing olefin π-complexes were carried out in an inert gas atmosphere with the use of absolute solvents. If a mixture of two or more products was formed, the individual compounds were isolated by preparative TLC on silica gel.

The IR spectra were recorded with an UR-10 spectrophotometer. The NMR spectra were measured with a Perkin-Elmer R-12 (60 MHz) spectrophotometer in $(CD_3)_2CO$, C_6D_6 and CS_2 with tetramethylsilane as an internal standard. The NMR ^{13}C spectra were recorded with a Bruker H-90 (22.63 MHz) spectrometer at room temperature. The internal standard was the signal of the solvent, i.e. cyclohexane (27.50 ppm). The mass spectra were obtained by means of a DS-50 spectrometer with an electron ionisation energy of 70 eV. A PRK-4 lamp employed as a source of ultraviolet light was placed 20—25 cm away from the solution, whose temperature during irradiation did not exceed 30°C.

Synthesis of $CH_2{=}CHSi(OMe)_3Fe(CO)_4$ (III). 1.48 g (10 mmol) vinyltrimethoxysilane and 3.64 g (10 mmol) $Fe_2(CO)_9$ in 50 ml hexane were stirred at 35—40°C for 2.5 hours. The solvent and volatile products were evaporated in vacuum. Freezing out from petroleum ether (b.p. 40—45°C) at —78°C gave 1.77 g of complex III (yield 55%). Complexes II, IV, V and IX were obtained likewise; IV and V were isolated by preparative TLC on silica gel.

Synthesis of $[(CH_2{=}CH)_4Si][Fe(CO)_3]_2$ *(VI).* To 1.52 g (5 mmol) of complex V in 50 ml cyclohexane was added 0.98 g (5 mmol) $Fe(CO)_5$ and the mixture was UV-irradiated for 7 hours while argon was passed through. The reaction mixture was filtered and the solvent evaporated from the filtrate in vacuum. Recrystallization from pentane gave 0.93 g (45%) of yellow crystals of VI, m.p. 73°C.

Synthesis of $(CH_2{=}CHSiMe_2OH)Fe(CO)_4$ *(X).* On addition of 2 ml water a solution of 2.0 g (7 mmol) (IX) in 30 ml ether was stirred for 1 hour at room temperature in an inert atmosphere. The organic layer was separated from the aqueous layer, washed with water until the reaction was neutral and dried over K_2CO_3. The solvent was eliminated in vacuum. Recrystallization from petroleum ether yielded 0.94 g (50%) of X, m.p. 44°C.

Synthesis of $[(CH_2{=}CHSiMe_2)_2O][Fe(CO)_4]_2$ *(XI).* On addition of 5 ml 3% HCl a solution of 2.0 g (7 mmol) of IX in 30 ml ether was refluxed for 2 hours in an inert atmosphere. The organic layer was separated from the aqueous fraction, washed with water until the reaction was neutral and dried over K_2CO_3. The solvent was emininated in vacuum. The yield of XI (a yellow oil) was 0.18 g (10%).

Synthesis of $[(CH_2{=}CHSiMe_2)_2]Fe(CO)_4$ *(XII) and* $[(CH_2{=}CHSiMe_2)_2]$*-*$[Fe(CO)_4]_2$ *(XIII).* 1.02 g (6 mmol) 1,2-divinyltetramethyldisilane and 2.18 g (6 mmol) $Fe_2(CO)_9$ in 50 ml hexane were stirred for 2.5 hours at room temperature in an inert atmosphere. The solvent was eliminated in vacuum and the residue separated by preparative TLC on silica gel with petroleum ether as an eluent. Separation gave 0.34 g (17%) of XII in the form of a yellow oil and 0.26 g (17%) of complex XIII as yellow crystals with m.p. 52—53°C (from pentane).

Synthesis of $[(CH_2{=}CHSiMe_2)_2O]Fe(CO)_4$ *(XV) and* $[(CH_2{=}CHSiMe_2)_2]$*-*$[Fe(CO)_4]_2$ *(XI).* 1.86 g (10 mmol) 1.3-divinyltetramethyldisiloxane and 7.28 g (20 mmol) $Fe_2(CO)_9$ in 60 ml hexane were stirred at 35—40°C for two hours. The solvent was eliminated in vacuum. Individual products XV and XI were isolated by TLC on silica gel with petroleum ether as an eluent. Both compounds are light yellow oils; the yields were 0.72 g (20%) of XV and 0.9 g (17%) of XI.

Synthesis of $[(CH_2{=}CHSiPh_2)_2O]Fe(CO)_4$ *(XVI) and* $[(CH_2{=}CHSiPh_2)_2O]$*-*$Fe(CO)_3$ *(XVIII).* 2.17 g (5 mmol) 1,3-divinyltetraphenyldisiloxane and 3.64 g (10 mmol) $Fe_2(CO)_9$ in 60 ml hexane were stirred at 35—40°C for two hours. The solvent and volatile products were eliminated in vacuum, the residual $Fe_2(CO)_9$ was filtered off and the reaction mixture separated by preparative TLC on silica gel with petroleum ether/benzene (4/1) as an eluent. The first fraction gave 0.6 g of a mixture of XVI and XVII in the ration 3 : 1; one more TLC run yielded 0.3 g (10%) of XVI in the form of a viscous yellow oil and 0.15 g of XVII which, according to ^1H NMR data, was contaminated with XVI. After recrystallization from pentane the second fraction obtained in the first TLC gave 0.31 g (11%) of XVIII, yellow crystals which decompose without melting above 65°C.

Synthesis of $[(CH_2{=}CHMeSiO)_4]Fe(CO)_4$ *(XIX).* 1.72 g (5 mmol) tetravinyltetramethylcyclotetrasiloxane and 1.82 g (5 mmol) $Fe_2(CO)_9$ in 60 ml hexane were stirred at 33—40°C for 2 hours. The solvent and volatile products were eliminated in vacuum. The residue after preparative TLC on silica gel with petroleum ether as an eluent yielded 1.02 g (40%) of XIX.

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