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Preliminary communication

CHEMISTRY OF ORGANOSILICON COMPOUNDS

CXLII*. ^{29}Si NMR SPECTRA OF SOME IRON AND RUTHENIUM COMPLEXES CONTAINING SILICON. REASSIGNMENT OF THE STRUCTURES OF THE COMPLEXES OBTAINED BY THE REACTION OF VINYLDISILANES AND NONACARBONYLDIIRON*

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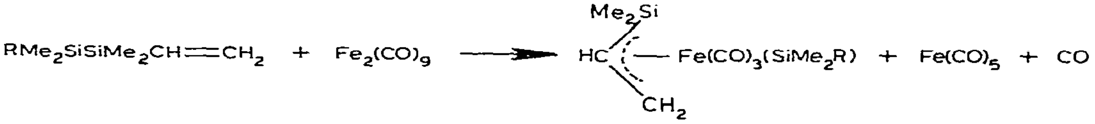
Summary

^{29}Si NMR studies on several iron and ruthenium carbonyl complexes containing silicon revealed that the complexes obtained from vinyldisilanes and nonacarbonyldiiron previously reported to be (η^3-1-silapropenyl)tricarbonyliron compounds really are (η^2-vinyldisilane)tetracarbonyliron complexes.

In a previous paper [2], we have described the reaction of vinylpentamethyldisilane (Ia) and 1,2-divinyltetramethyldisilane (Ib) with nonacarbonyldiiron to give very reactive and air-sensitive (η^3-1,1-dimethyl-1-silapropenyl)(trimethylsilyl)tricarbonyliron (IIa) and (η^3-1,1-dimethyl-1-silapropenyl)(dimethylvinylsilyl)tricarbonyliron (IIb), respectively.



(Ia) R = Me
(Ib) R = $CH_2{=}CH$

(IIa) R = Me
(IIb) R = $CH_2{=}CH$

The η^3-1-silapropenyl structure of II was proposed on the basis of various spectroscopic studies [2]. We concluded that the available evidence suggested strongly the presence of the η^3-1-silapropenyl ligand in II, but ultimate proof

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*For part CXLI, see ref. [1].

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of the structure should be given by an X-ray crystal structure determination. Since then, we have prepared a number of such iron complexes and examined some reactions [3], but unfortunately no compound suitable for an X-ray crystal structure determination has been obtained.

On the other hand, the recent development of Fourier transform NMR has reduced experimental difficulties in ^{29}Si NMR studies [4], so that we have studied the ^{29}Si NMR spectra of the complexes in the hope of elucidating the structure. Since there is only a limited number of ^{29}Si NMR data for transition metal complexes of organosilicon compounds [5], we have measured the ^{29}Si NMR spectra of several kinds of iron and ruthenium complexes containing silyl group(s) to obtain a general trend in the ^{29}Si NMR chemical shifts. The results are listed in Table 1.

TABLE 1

^{29}Si NMR CHEMICAL SHIFTS OF SOME ORGANOSILICON COMPOUNDS INCLUDING IRON CARBONYL AND RUTHENIUM CARBONYL COMPLEXES [a]

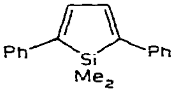
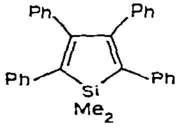
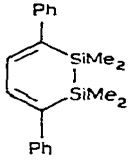
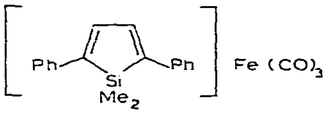
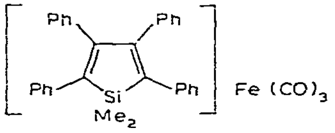
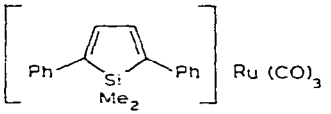
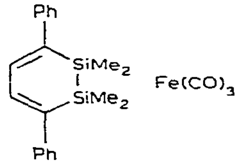
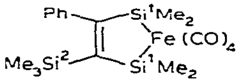
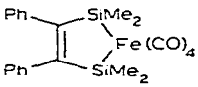
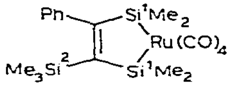
Compounds	Chemical shift (ppm)	
	Si^1	Si^2
Me_4Si	0.00	
$PhSiMe_3$	−4.12 (lit. −4.50) [6] [b]	
$Me_3SiSiMe_3$	−19.16 (lit. −19.58) [6] [b]	
$CH_2{=}CHSi^1Me_2Si^2Me_3$ (Ia)	−23.96	−19.16
$CH_2{=}CHSiMe_2SiMe_2CH{=}CH_2$ (Ib)	−24.14	
$CH_2{=}CHSi^1Me_2Si^2Me_2C_6H_4$-*p*-t-Bu (Ic)	−24.08	−22.05
$CH_2{=}CHSiMe_3$ (IVa)	−6.60 (lit. −6.80) [6] [b]	
$CH_2{=}CHSiMe_2OEt$ (IVb)	+4.49	
 (VIa)	+2.27	
 (VIb)	+8.14	
 (IX)	−32.25	
$(Me_3SiCH{=}CH_2)Fe(CO)_4$ (Va)	+4.43	
$(EtOSiMe_2CH{=}CH_2)Fe(CO)_4$ (Vb)	+10.57	
$(Me_3Si^2Si^1Me_2CH{=}CH_2)Fe(CO)_4$ (IIIa)	−11.40	−18.58
$(CH_2{=}CHSi^2Me_2Si^1Me_2CH{=}CH_2)Fe(CO)_4$ (IIIb)	−11.70	−23.77
$(p\text{-t-BuC}_6H_4Si^2Me_2Si^1Me_2CH{=}CH_2)Fe(CO)_4$ (IIIc)	−11.55	−21.55
$(\eta^5\text{-}C_5H_5)Fe(CO)_2SiMe_3$ (XI)	+41.86 (lit. +41.23) [5] [b]	
$(\eta^5\text{-}C_5H_5)Fe(CO)_2Si^1Me_2Si^2Me_3$ (XII)	+17.63	−11.08

TABLE 1 (continued)

Compounds	Chemical shift (ppm)	
	Si^1	Si^2
 (VIIa)	+8.78	
 (VIIb)	+17.66	
 (VIII)	+15.18[c]	
 (X)	−18.43	
 (XIII)	+45.39 +48.83	−7.65
 (XIV)	+48.16	
 (XV)	+32.40 +34.68	−7.92

[a] ^{29}Si NMR spectra were measured at 39.74 MHz on a Varian XL-200 Spectrometer in proton gated decoupled mode. The spectral measurements were made using carbon disulfide as a solvent in a co-axial 10 mm sample tube, containing a 5 mm o.d. tube of deuteriobenzene for the internal deuterium field/frequency lock. The ^{29}Si chemical shift in ppm are internally referenced to the ^{29}Si signal of tetramethylsilane and obtained either by direct measurement of the solution containing tetramethylsilane or calibration of the shift of the signal by means of the transmitter frequency. [b] Values in the references are converted to those in the Me$_4$Si scale. [c] For the solution containing a relaxation agent, chromium(III) acetylacetonate [Cr(acac)$_3$].

In addition to IIa and IIb, a complex derived from 1-vinyl-2-(*p*-*t*-butylphenyl)-1,1,2,2-tetramethyldisilane (Ic) was examined. The latter was isolated in the form of low-melting crystals and was relatively stable toward air and moisture.

As a result of the present study, it became clear that the (vinyldisilane)iron carbonyl complexes previously reported to be (η^3-1-silapropenyl)tricarbonyliron complexes (II) really are (η^2-vinyldisilane)tetracarbonyliron species (III).

$(RMe_2SiSiMe_2CH{=}CH_2)Fe(CO)_4$

(IIIa) R = Me
(IIIb) R = $CH_2{=}CH$
(IIIc) R = p-t-$C_4H_9C_6H_4$

The ^{29}Si chemical shifts for compounds containing more than two silicon atoms are assigned so as to remain consistent with substituent effects. The assignments in Table 1 seem to be reasonable; unfortunately, the two low field silicon signals for both XIII and XV cannot be distinguished from each other.

Two major features may be pointed out from the data of Table 1. First, very large downfield shifts in the range of 32—48 ppm relative to Me_4Si are observed for silicon atoms bound directly to iron and ruthenium in XIII, XIV and XV as previously reported for XI [5]. In XII the ^{29}Si chemical shift was found at +17.63 ppm, but if one takes the upfield effect due to the second silicon atom of the disilane moiety of around 17—19 ppm into consideration, the downfield effect of the metal may be estimated at 34—36 ppm. Second, iron and ruthenium complexes of vinylsilanes and dienylsilanes exhibit moderate downfield shifts for the silicon atoms relative to the parent compound in the range of 6 to 14 ppm. Table 2 summarizes the data of the induced shift. The average induced shifts for two silicon atoms in IIIa, IIIb and IIIc are 12.51 ± 0.07 and 0.48 ± 0.11 ppm, respectively. The 12.51 ppm shift for a silicon atom is compatible with the silicon atom of η^2-vinylsilane complexes as seen in Va and Vb and virtually no shift, as observed for the second silicon atom, is inconsistent with structure II, where a silicon atom is bound directly to iron and should therefore show a large downfield shift.

Since the previous assignment of the structures IIa and IIb was based largely on the mass spectroscopic data that counted *m/e* 298 and 310 as molecular ions corresponding to the tricarbonyliron complexes, we have reexamined the mass spectra of these complexes.

A mass spectrum of IIIc taken at 10 eV with an ion source temperature of about 150°C showed a weak molecular ion at *m/e* 444 (~10%) corresponding to $(p\text{-t-}C_4H_9C_6H_4SiMe_2SiMe_2CH{=}CH_2)Fe(CO)_4$ and a base peak at *m/e* 276. The relative intensity of the parent peak changed with the condition of the experiment and was not very reproducible. However, the existence of the parent peak at *m/e* 444 for IIIc is beyond a possibility of doubt. For IIIa, it was still more difficult to observe the parent peak, but again the mass spectrum taken at low accelerating voltage (~10 eV) with a low ion source

TABLE 2

INDUCED PARAMAGNETIC SHIFTS (Δδ) FOR VINYL- AND DIENYLSILANES ON COMPLEXATION WITH IRON AND RUTHENIUM

Complex	Δδ (ppm)		Complex	Δδ (ppm)	
	Si^1	Si^2		Si^1	Si^2
Va	+11.03		IIIa	+12.56	+0.58
Vb	+6.08		IIIb	+12.44	+0.37
VIIa	+6.51		IIIc	+12.53	+0.50
VIIb	+9.52				
VIII	+12.91				
X	+13.82				

temperature showed a recognizable peak corresponding to the parent peak of the tetracarbonyliron complex.

Other physical properties, spectral data and elemental analysis reported previously for (vinyldisilane)iron carbonyl complexes [2] are compatible with the structure of both II and III, but the data reported in this paper lead to the conclusion that the products obtained by the reaction of vinyldisilanes and nonacarbonyldiiron should be (η^2-vinyldisilane)tetracarbonyliron complexes (III)*.

We have also interpreted the thermolysis and photolysis of vinyldisilanes in the presence of $Fe(CO)_5$ [3] and ring contraction reaction of X [8] in terms of the intermediate (η^3-1-silapropenyl)tricarbonyliron complexes. Although the complexes isolated were not (η^3-1-silapropenyl)tricarbonyliron, it is still possible that such a complex can be an intermediate.

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*J.S. McKennis et al. [7] have recently obtained the same conclusion.