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REACTIONS OF A (η^3-VINYLCARBENE)IRON COMPLEX WITH DIAZO COMPOUNDS: FORMATION OF (η^4-BUTADIENE)IRON DERIVATIVES

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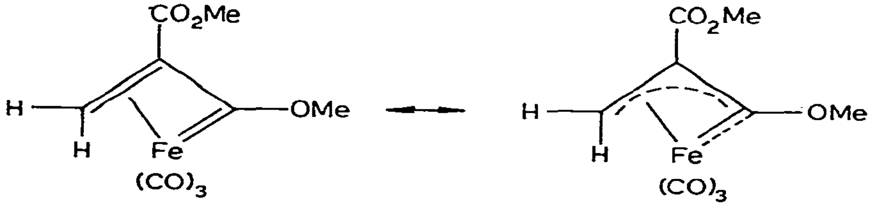
Summary

A (η^3-vinylcarbene)tricarbonyliron complex I reacted with diazo compounds affording (η^4-butadiene)tricarbonyliron complexes (Va—Vc) by the insertion of the methylene group of the diazo compounds into the carbene carbon—iron bond [or by the coupling of the methylene group with the carbene carbon of the complex I].

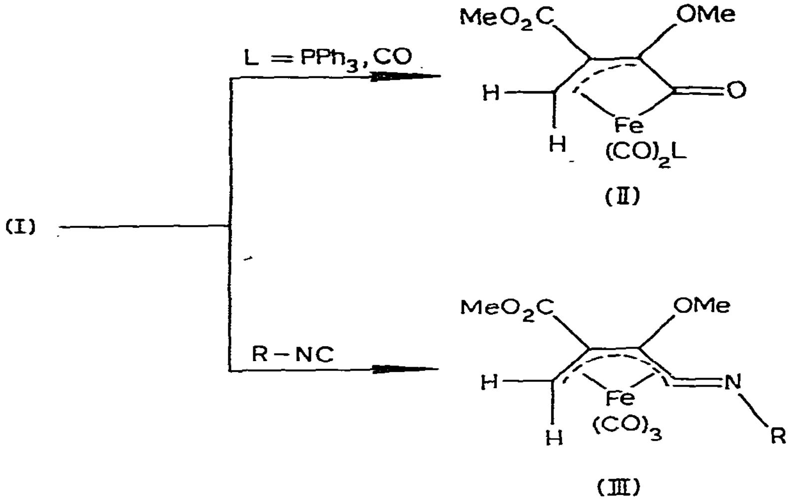
Introduction

The chemistry of carbene-transition metal complexes has been extensively developed since the first report of such a complex by E.O. Fischer [1]. Recently, the first η^3-vinylcarbene iron complex (I), in which both the adjacent olefinic group and the carbene carbon are coordinated to the iron atom, was prepared by the alkylation of an η^3-acryloyliron complex [2] and X-ray analysis showed an unusually distorted structure [3]. It was shown that I reacts with Lewis bases such as tertiary phosphines, carbon monoxide and isonitriles to afford η^4-vinylketene-iron complexes (II) [4], or η^4-vinylketenimine-iron complexes (III) [5] (Scheme 1), respectively. These reactions show that complex I



(I)

SCHEME 1

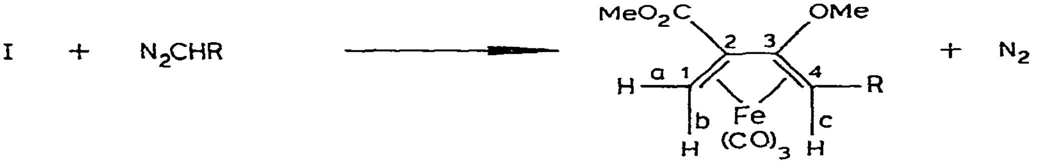


is readily attacked by nucleophile reagents. We now report the reactions of complex I with diazo compounds such as diazomethane (IVa), phenyldiazomethane (IVb) or ethyl diazoacetate (IVc).

Results and discussion

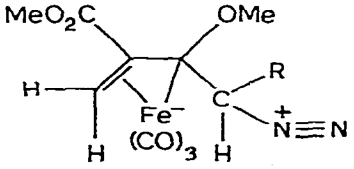
The η^3-vinylcarbene complex I reacted with gaseous diazomethane in diethyl ether solution at room temperature. Work-up gave yellow crystals of Va (cf. Scheme 2) in 49% yield. Complex Va was diamagnetic and stable in air for several hours. Its molecular weight and analytical data (Table 1) show that one CH_2 moiety has been added to I to form Va. On the basis of the following spec-

SCHEME 2



(IVa, R = H;
IVb, R = Ph;
IVc, R = CO_2Et)

Va, R = H^d;
Vb, R = Ph;
Vc, R = CO_2Et)



(VI)

tral data, Va was demonstrated to be tricarbonyl(η^4-2-methoxy-3-methoxycarbonylbuta-1,3-diene)iron (Scheme 2). The IR spectrum of Va (Table 2) shows strong ν(C≡O) absorptions at 2060 and 1970(br) cm^{-1} and a strong ν(C=O/ ester) at 1720 cm^{-1}. The ^{1}H NMR spectrum of Va shows four olefinic proton signals at δ —0.24, 0.20, 2.08 and 2.26 ppm (Table 3), showing that the olefinic

TABLE 1

ANALYTICAL DATA OF COMPLEXES Va—Vc

Complex	Color	Yield (%)	Mol. wt. [a] calcd.	M.p. (°C)	Analyses, found (Calcd.) (%)	
					C	H
Va	yellow crystals	49	296 (282)	35	42.2 (42.6)	3.57 (3.57)
Vb	yellow crystals	28	330 (358)	126 (decomp.)	53.8 (53.7)	3.84 (3.94)
Vc	red oil	21	354 [b] (354)	—	43.7 (44.1)	4.26 (3.99)

[a] By cryoscopy in benzene. [b] By mass spectroscopy.

TABLE 2

IR SPECTRAL DATA OF Va—Vc (cm^{-1})

Complex	ν(C≡O)		Other bands
	Metal carbonyl region	Ester	
Va [a]	2060 1970(br)	1720	
Vb [a]	2050 1990(br)	1720	1600 1500 750 690 } phenyl
Vc [b]	2080 2010(br)	1740(br)	

[a] KBr disk. [b] Liquid film.

TABLE 3

^{1}H NMR SPECTRAL DATA OF Va—Vc (δ, ppm, J, Hz, CDCl$_3$)

Complex	Olefinic proton	OMe	Other resonances
Va	—0.24 (d, 3.0, 1 H); H^b [b] 0.20 (d, 5.4, 1 H); H^c 2.08 (d, 3.0, 1 H): H^a 2.26 (d, 5.4, 1 H); R = H^d	3.66 (s, 3 H) 3.85 (s, 3 H)	
Vb [a]	0.02 (d, 3.3, 1 H); H^b 1.81 (s, 1 H); H^c 2.03 (d, 3.3, 1 H): H^a	3.79 (s, 3 H) 3.89 (s, 3 H)	7.24 (s, 5 H); -Ph
Vc [a]	—0.06 (d, 3.3, 1 H); H^b 0.76 (s, 1 H); H^c 1.98 (d, 3.3, 1 H); H^a	3.79 (s, 6 H)	1.20 (t, 7.2, 3 H) 4.08 (q, 7.2, 2 H) } -Et

[a] Benzene and dichloromethane were used for internal reference for Vb and Vc, respectively, and the chemical shifts were calculated into the δ value. [b] See text.

TABLE 4

^{13}C NMR SPECTRAL DATA OF Va—Vc (δ, ppm, J Hz, $CDCl_3$)

Complex	Olefinic carbon	OMe	CO_2Me	Fe—CO	Other resonances
Va	30.4 (dd, 153.3, 164.1); C^1 [a]	52.0	169.7	208.7	
	33.7 (t, 161.1); C^4	56.6			
	74.5 (d, 8.0); C^2				
	143.0 (s); C^3				
Vb	32.2 (t, 161.1); C^1	52.6	169.9	209.0	128.4 (d, 162.1) -Ph
	61.0 (d, 156.3); C^4	61.2			128.7 (d, 162.1) -Ph
	79.1 (s); C^2				131.2 (d, 162.1) -Ph
	137.6 (s); C^3				134.5 (s) -Ph
Vc	32.2 (t, 162.1); C^1	52.6	169.6	211.9	13.9 (q, 126.0); $-CH_2CH_3$
	46.4 (d, 162.1); C^4	58.7			61.4 (t, 117.0); $-CH_2CH_3$
	77.4 (d, 6.0); C^2				168.8 (s); $-CO_2Et$
	138.8 (s); C^3				

[a] See Scheme 2.

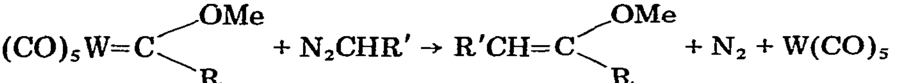
groups are coordinated to the iron atom. In general, signals for H^b and H^c protons (see Scheme 2) in (η^4-butadine)tricarbonyliron complexes are found at higher field than those of H^a and H^d protons [6]. Comparing with the ^1H NMR spectrum of $Fe[CH_2=CHC(OMe)=CH_2](CO)_3$ [7], signals at —0.24 and 0.20 ppm are assigned to the H^b and H^c protons and those at δ 2.08 and 2.26 ppm to the H^a and H^d protons, respectively. The ^{13}C NMR spectrum of Va (Table 4) shows four signals of the butadiene skeleton coordinated to the iron at δ 30.4 (dd, $J(CH) = 153.3$, 164.1 Hz, C^1), 33.7 (t, $J(CH) = 161.1$ Hz, C^4), 74.5 (d, $J(CCH) = 8.0$ Hz, C^2) and 143.0 ppm (s, C^3).

Phenyldiazomethane (IVb) also reacted with I in ether at room temperature to give yellow crystals of Vb in 28% yield. Spectroscopic data showed Vb to be the phenyl derivative of Va. The ^1H NMR spectrum of Vb showed three olefinic proton resonances at δ 0.02 (d, $J = 3.3$ Hz), 1.81 (s), 2.03 (d, $J = 3.3$ Hz) ppm. These were assigned to H^b, H^c, and H^a (Scheme 2), respectively. The chemical shift of H^c which is found at higher field than that of H^d in Va shows that the phenyl group is oriented as shown in the Scheme 2. In this reaction *trans*-stilbene was produced as a by-product in 21% yield.

Complex I also reacted with ethyl diazoacetate (IVc) in dichloromethane, to produce Vc as a red oil which could be isolated by column chromatography on silica gel in 21% yield.

Complex I reacted with dimethyl diazomalonate, but no product containing the organic group was isolated.

These results show that reactions of I with diazo compounds afford novel (η^4-butadiene)iron derivatives. In the reaction of I with tertiary phosphines the insertion of a carbonyl group into the carbene carbon—iron bond and the coordination of the ligand to an iron atom was observed (Scheme 1) [4]. But in the reaction of I with diazo compounds, it appears that the carbene carbon of I couples with the methylene carbon of the diazo compound at the iron atom to afford Va—Vc. The attack of the nucleophile at the carbene carbon also has been observed in the reaction of I with isonitriles [5]. The reaction can be explained by the mechanism proposed by Casey for the reaction of a carbene complex (VII) with diazo compounds, a process which produces olefins (eq. 3) [8]. The reaction may proceed via an intermediate (VI) derived by nucleophilic



$$(CO)_5W{=}C(OMe)R + N_2CHR' \rightarrow R'CH{=}C(OMe)R + N_2 + W(CO)_5 \qquad \text{(eq. 3)}$$

(VII)

attack of the diazo compound which subsequently fragments to form a η^4-butadiene complex and dinitrogen (Scheme 2).

The decomposition of complex Va with trimethylamine oxide was attempted. Although the formation of the free ligand was observed by GLC, the diene could not be isolated by distillation or by column chromatography, probably due to the polymerization.

In conclusion, the reaction of the η^3-vinylcarbene iron complex I with diazo compounds provides a novel synthesis of η^4-butadiene iron complexes.

Experimental

All of experiments were performed under an atmosphere of argon or nitrogen. IR spectra were recorded on a Hitachi EPI-G2 grating spectrometer. ^1H NMR spectra were obtained on JEOL-JNM-FX-100 instruments. ^{13}C NMR spectra were recorded on a JEOL-JNM-FX-100 spectrometer at 25.05 MHz. Molecular weights were determined by the cryoscopic method in benzene, or by mass spectrometry. Solvents were dried by published techniques and were distilled in an atmosphere of argon before use. Tricarbonyl[1,3-η^3-2-methoxycarbonylvinyl(methoxy)carbene]iron I [2], diazomethane [9], phenyldiazomethane [10], ethyl diazoacetate [11], and dimethyl diazomalonate [12] were prepared by literature methods.

Reaction of I with diazomethane

Into the solution of I (3 mmol) in 50 ml of dry diethyl ether was bubbled an excess of diazomethane gas in a stream of nitrogen at room temperature. After evaporation of the solvent, the residual solid was extracted through a glass filter by two 10-ml portions of dry n-hexane. The filtrate was concentrated and cooled to —78°C to afford yellow crystals of complex Vb in 49% yield.

Reaction of I with phenyldiazomethane

To the solution of I (3 mmol) in 50 ml of dry diethyl ether was added a diethyl ether solution of phenyldiazomethane (3 mmol) at —78°C, and then the reaction solution was agitated for 2 h at room temperature. After evaporation of the solvent, the residual solid was extracted with two 10-ml portions of 1/1 n-hexane/diethyl ether and the extracts were filtered. The filtrate was concentrated under vacuum. The residual oil was dissolved in 3 ml of benzene and chromatographed on silica gel. Elution with benzene gave *trans*-stilbene (21%) and then elution with benzene/diethyl ether (1/1) gave yellow crystals of Vb in 28% yield.

Reaction of I with ethyl diazoacetate

To the solution of I (3 mmol) in 10 ml of dry dichloromethane was added ethyl diazoacetate (3 mmol) at −78°c, and the mixture was agitated for 1 h at room temperature. After evaporation of the solvent, the residue was dissolved in 2 ml of benzene and chromatographed on silica gel. Elution with benzene/diethyl ether (1/1) gave Vc as a red oil in 21% yield.

Acknowledgement

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References

1 For example, E.O. Fischer, R.B.A. Pardy and U. Schubert, J. Organometal. Chem., 181 (1979) 37, and references cited therein; C.P. Casey in D. Seyferth (Ed.), New Applications of Organometallic Reagents in Organic Synthesis, Elsevier, Amsterdam, 1976, P397.
2 T. Mitsudo, Y. Watanabe, H. Nakanishi, I. Morishima, T. Inubushi and Y. Takegami, J. Chem. Soc. Chem. Commun., (1976) 416; J. Chem. Soc. Dalton, (1978) 1298.
3 K. Nakatsu, T. Mitsudo, H. Nakanishi, Y. Watanabe and Y. Takegami, Chem. Lett., (1977) 1447.
4 T. Mitsudo, T. Sasaki, Y. Watanabe, Y. Takegami, S. Nishigaki and K. Nakatsu, J. Chem. Soc. Chem. Commun., (1978) 252.
5 T. Mitsudo, H. Watanabe, Y. Komiya, Y. Watanabe and Y. Takegami, J. Organometal. Chem., 190 (1980) C39.
6 G.F. Emerson, J.E. Mahler, R. Kohhar and R. Pettit, J. Org. Chem., 29 (1964) 3620.
7 R.E. Graf and C.P. Lillya, J. Organometal. Chem., 122 (1976) 377.
8 C.P. Casey, S.H. Bertz and T.J. Burkhart, Tetrahedron Letters, (1973) 1421.
9 Th.J. de Boer and H.J. Backer, Org. Syntheses, Coll. Vol. 4 (1963) 250.
10 R.J. Mohrbacher and N.H. Cromwell, J. Amer. Chem. Soc., 79 (1957) 401.
11 N.E. Searle, Org. Syntheses, Coll. Vol. 4 (1963) 424.
12 B.W. Peace, F. Carman and D.S. Wulfman, Synthesis, 1 (1971) 658.