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SYNTHESES OF σ-CYCLOBUT-1-EN-3-ONYL COMPLEXES BY CYCLOADDITION OF KETENES TO SOME TRANSITION METAL ALKYNYL COMPLEXES

PANGBU HONG *

The Institute of Physical and Chemical Research, Wako-shi, Saitama 351 (Japan)

KENKICHI SONOGASHIRA and NOBUE HAGIHARA

The Institute of Scientific and Industrial Research, Osaka University, Suita, Osaka 565 (Japan)

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Summary

Reactions of ketenes ($R^1R^2C{=}C{=}O$) with (η^5-C_5H_5)Ni(PPh_3)—C≡CR (I) and (η^5-C_5H_5)Fe(CO)(L)—C≡CR (III, L = CO and PPh_3) give σ-cyclobut-1-en-3-onyl complexes, {(η^5-C_5H_5)Ni(PPh_3)—$\overline{C{=}C(R)COC}R^1R^2$ (VI) and (η^5-C_5H_5)Fe(CO)(L)—$\overline{C{=}C(R)COC}R^1R^2$ (IX)}, (2 + 2) cycloaddition products, in good yields. The σ-cyclobutenonyl complexes also can be prepared by the reaction of I and III with acyl chlorides in the presence of triethylamine.

Introduction

We have demonstrated previously that the reactions of the ethynyl complex (η^5-C_5H_5)Ni(PPh_3)—C≡CH (Ia) with aryl isocyanates give linear adducts, (η^5-C_5H_5)Ni(PPh_3)—C≡CCONHR (II), which are formed by insertion of isocyanates into the acetylenic C—H bond [1]. We have suggested that the formation of the complex II proceeds via a dipolar intermediate resulting from electrophilic attack of isocyanates on the ethynyl group [1]. Recently it has been reported that the reaction of (η^5-C_5H_5)Fe$(CO)_2$—C≡CPh (IIIa) with electrophiles such as tetracyanoethylene and hexafluoroacetone gave (2 + 2) cycloaddition products [2]. In this paper we wish to report that the reactions of alkynyl complexes such as I and III with ketenes also lead to (2 + 2) cycloaddition products, specifically, σ-cyclobut-1-en-3-onyl complexes. Although the σ-cyclobutenonyl-iron complex IV has recently been prepared by the reaction of V with triethylamine [3], our reaction may offer a simple and convenient synthetic method for σ-cyclobut-1-en-3-onyl complexes.

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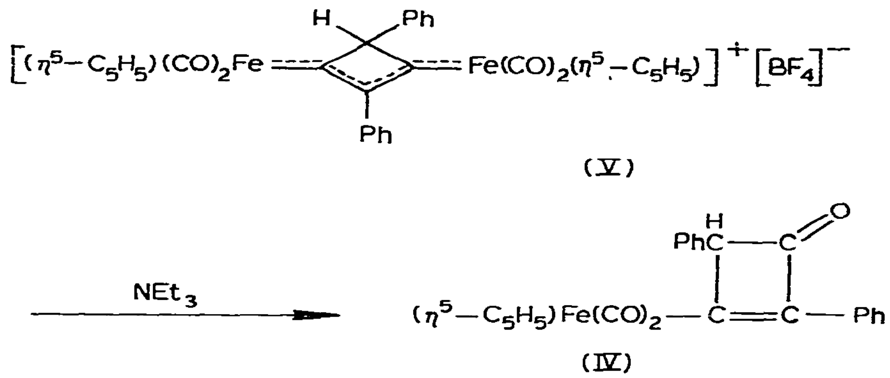
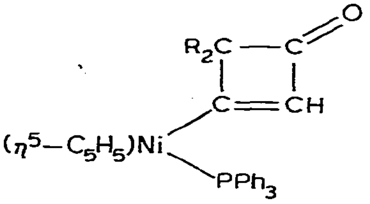


(V)

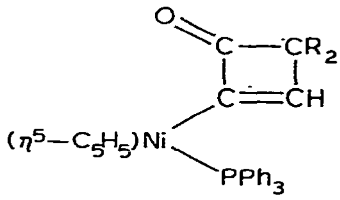
(IV)

Results and discussion

Treatment of Ia with diphenylketene in benzene at room temperature for two days gave a brownish-green solution, from which a green crystalline complex was isolated in a 32% yield, together with a small amount of $Ni(CO)_2(PPh_3)_2$. Elemental analysis and molecular weight measurement indicated that the green complex was a 1/1 adduct of Ia and the ketene. The infrared spectrum of the 1/1 adduct has no band assignable to $\nu(C{\equiv}C)$, but does show a band assignable to $\nu(C{=}O)$ at 1704 cm^{-1}. The ^1H NMR spectrum shows two singlets assignable to cyclopentadienyl and olefinic protons at δ 4.89 (5 H) and 5.89 ppm (1 H), respectively. These spectroscopic data support a cyclic σ-cyclobutenonyl structure, which may be either VIa or VII as formulated below, for the 1/1 adduct.



(VIa, R = Ph; VIb, R = H)



(VII)

The ^1H NMR spectrum of the product (VIb) from Ia and ketene ($CH_2{=}C{=}O$) gives further information on the structure. The spectrum shows two singlets assignable to olefinic and methylene protons at δ 5.73 and 2.81 ppm, relative intensity 1 : 2, in addition to the signals due to triphenylphosphine and the cyclopentadienyl groups. The absence of coupling between these signals indicates that the adduct is the σ-cyclobut-1-en-3-onyl complex (VIb).

Similarly, the substituted ethynyl complexes (Ib—If) reacted with diphenylketene, methylphenylketene, and ketene to give σ-cyclobutenonyl complexes (VI) in good yields. These results are summarized in Table 1.

TABLE 1

$(\eta^5\text{-}C_5H_5)Ni(PPh_3)\text{—}\overline{C{=}C(R^1)COC}(R^2)(R^3)$

	R^1	R^2	R^3	Mp. (°C) [c]	Yield (%)	^1H NMR (δ, ppm) [d]		IR (cm^{-1}) [f] ν(C=O)
						$\eta^5\text{-}C_5H_5$	Others [e]	
VIa	H	Ph	Ph	120	32 [a]	4.89	5.89 (=CH, s)	1700
VIb	H	H	H	145	27 [a]	5.18	5.73 (s, =CH), 2.81 (s, CH_2)	1690
VIc	Ph	Ph	Ph	108—109	78 [a]	5.12		1704
VId	Ph	H	H	148—149	84 [a]	5.27	2.64 (s, CH_2)	1690
VIe	$p\text{-}CH_3C_6H_4$	Ph	Ph	122—124	80 [a]	5.09	2.30 (s, CH_3)	1700
VIf	$p\text{-}BrC_6H_4$	Ph	Ph	131—133	62 [a]	5.11		1690
VIg	$CH{=}CH_2$	Ph	Ph	135—137	70 [a]	4.97	5.89 (d, 12 Hz), 5.76 (d, 6 Hz)	1697
VIh	CH_3	Ph	Ph	164—165	82 [a]	4.92	1.20 (s)	1700
VIi	H	Ph	CH_3	141—143	72 [a]	4.91	5.72 (s, =CH), 1.46 (s, CH_3)	1710
VIk	Ph	Ph	H	150—152	73 [b]	4.96	3.60 (d, 1 Hz)	1713
VIl	Ph	CH_3	H	152—153	68 [b]	5.27	2.50 (q, 7 Hz), 1.05 (d, 7 Hz)	1695

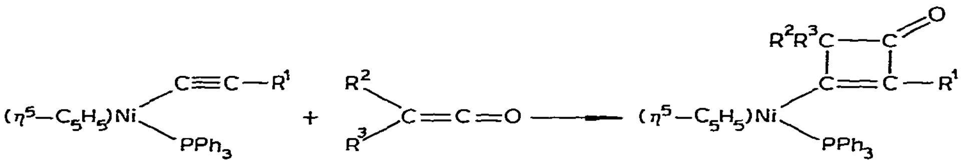
[a] By the reaction of a ketone with I. [b] By the reaction acetyl chlorides with I in the presence of triethylamine. [c] With decomposition. [d] In $CDCl_3$. [e] Signals due to aromatic protons were omitted. [f] KBr pellets.

TABLE 2

$(\eta^5\text{-}C_5H_5)(CO)(L)Fe\text{-}\overline{C{=}C(R)COC}Ph_2$ (VIII)

	R	L	Color	M.p. (°C)	Yield (%)	IR [a] (cm^{-1})		^1H NMR [b] (δ, ppm)	
						ν(C≡O)	ν(C=O)	C_5H_5	Others
VIIIa	Ph	CO	yellow	189—190	80	2035, 1982	1711	4.46	7.1—7.95 (Ph)
VIIIb	Ph	PPh_3	red	160—162	70	1950	1693	4.19	6.5—7.8 (Ph)
VIIIc	CH_3	CO	yellow	178—179	95	2035, 1983	1710	4.58	2.72 (Ph), 2.0 (CH_3)

[a] KBr pellet. [b] In $CDCl_3$.



(2)

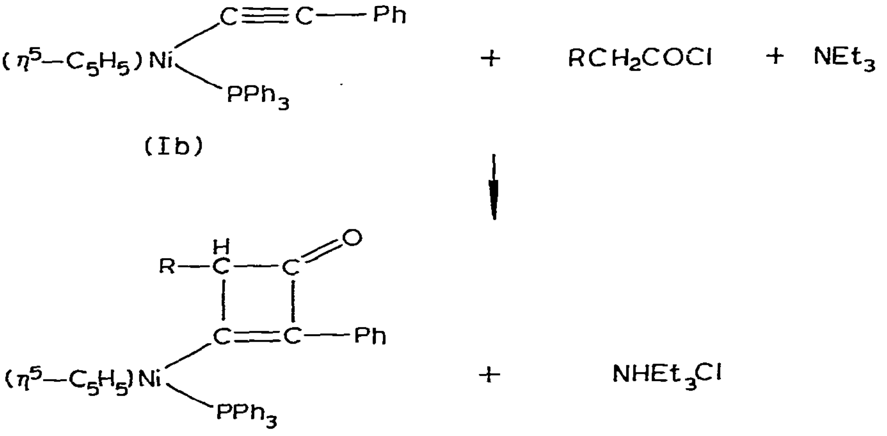
(Ia, R^1 = H;
Ib, R^1 = Ph;
Ic, R^1 = p-$CH_3C_6H_4$;
Id, R^1 = p-BrC_6H_4;
Ie, R^1 = $CH{=}CH_2$;
If, R^1 = CH_3)

$R^2 = R^3 = Ph$
$R^2 = Ph$, $R^3 = CH_3$
$R^2 = R^3 = H$

(VI)

It is noteworthy that the cycloaddition of diphenylketene to the vinylethynyl complex (Ie) takes place at the acetylenic rather than the olefinic bond, in analogy with cycloaddition of dimethylketene to but-1-en-3-ynyl ether [4].

As unstable monosubstituted ketenes are generated by dehydrochlorination of acetyl chlorides (RCH_2COCl) with tertiary amines [5], we examined the reactions of I with the chlorides in the presence of triethylamine, and found that the reactions also give cyclic adducts of monosubstituted ketenes in good yields. When phenylacetyl and propionyl chlorides were added to a mixture of Ib and triethylamine, the adducts of phenylketene and methylketene were obtained in 73 and 68% yields, respectively.

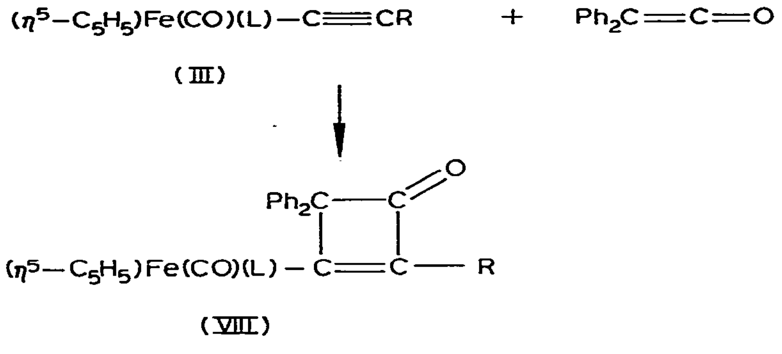


(Ib)

(3)

(VIk, R = Ph;
VIl, R = CH_3)

Similarly, the σ-cyclobutenonyl-iron complexes, VIII, were prepared from the alkynyl-iron complexes, III. From $(\eta^5\text{-}C_5H_5)Fe(CO)_2{-}C{\equiv}CPh$ (IIIa) and diphenylketene, $(\eta^5\text{-}C_5H_5)Fe(CO)_2{-}C{=}C(Ph)COCPh_2$ (VIIIa) was obtained in an 80% yield. $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3){-}C{\equiv}CPh$ (IIIb) and $(\eta^5\text{-}C_5H_5)Fe(CO)_2{-}C{\equiv}CCH_3$ (IIIc) also gave the corresponding adducts, VIIIb and VIIIc, in 70 and 95% yield, respectively. These results are shown in Table 2. The known σ-butenonyl complex IV [3] was also obtained by the reaction of IIIa with phenylacetyl chloride in the presence of triethylamine in 87% yield.

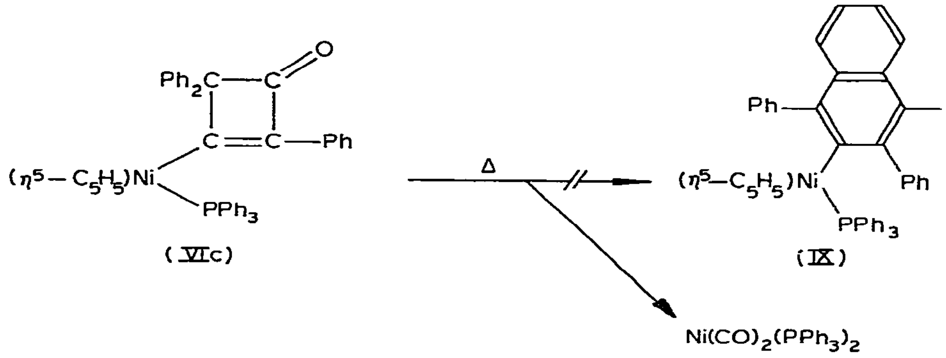


L = CO and PPh_3
R = Ph and CH_3

(4)

VIIIa—VIIIc are air stable in the solid state. The infrared spectrum of VIIIa shows two metal carbonyl absorptions at 2035 and 1982 cm^{-1} and a ketonic carbonyl absorption at 1711 cm^{-1}. These absorptions are similar to those of IV, which has $\nu(C\equiv O)$ at 2025 and 1980 cm^{-1} and $\nu(C=O)$ at 1705 cm^{-1} [3]. The ^1H NMR spectrum contains complex band at δ 7.1—7.95 ppm and a singlet peak at δ 4.46 ppm in a relative intensity 15 : 5, attributable to phenyl and cyclopentadienyl protons, respectively.

Diphenylketene reacts with phenylacetylene to give 3,4-diphenyl-1-napthol [6]. On the other hand, the reaction of the ketene with ethoxyacetylene at low temperature gives a cyclobutenone, which can be converted into the derivative of naphthol by warming [7]. An attempt to obtain the naphthol IX by heating VIc at 110—120° C give the decomposition product $Ni(CO)_2(PPh_3)_2$ in 56% yield. No organic residues could be isolated.



(5)

The formation of $Ni(CO)_2(PPh_3)_2$ indicates that the nickel metal eliminated the carbonyl group from the cyclobutenonyl ligand in the course of decomposition of VIc. Because $Ni(CO)_2(PPh_3)_2$ is formed by the reaction of the alkyl complex $(\eta^5\text{-}C_5H_5)Ni(PPh_3)R$ with diphenylketene or isocyanates [8], it seems that the decarbonylation probably proceeds intermolecularly. $Ni(CO)_2(PPh_3)_2$ is also obtained as a by-product of the reaction of diphenylketene with the alkynyl complex I. It might be generated by the decomposition of VI. In fact, when a solution of VIc in benzene was allowed to stand at room temperature for three weeks, the complex was completely decomposed to give $Ni(CO)_2(PPh_3)_2$. On the other hand, the iron complex VIII is thermally stable at 120° C.

Experimental

All reactions were carried out under an atmosphere of nitrogen. Melting points were taken on a micro-melting point apparatus, Yanagimoto MP-S2, and are uncorrected. Infrared spectra were recorded on a Jasco DS-402G spectrophotometer. ^1H NMR spectra were obtained on Hitachi Perkin Elmer R-20 and Varian HA-100B spectrometers using tetramethylsilane as an internal reference. Molecular weights were measured on a Mechrolab pressure osmometer in benzene or chloroform. The alkynyl complexes $\{(\eta^5\text{-}C_5H_5)Ni(PPh_3)\text{—}C{\equiv}CR$ [9], $(\eta^5\text{-}C_5H_5)Fe(CO)(L)\text{—}C{\equiv}CPh$ [10], $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{—}C{\equiv}CCH_3$ [11]} and diphenylketene [12], methylphenylketene [13], and ketene [14] were prepared according to published methods.

Reaction of $(\eta^5\text{-}C_5H_5)Ni(PPh_3)\text{—}C{\equiv}CPh$ (Ib) with diphenylketene

To a solution of Ib (1.45 g, 3 mmol) in benzene (20 ml) was added diphenylketene (0.8 ml) at room temperature. After it had stood for 2 days, the brownish-green solution was evaporated under reduced pressure, and the residue was subjected to column chromatography on alumina (Sumitomo activated alumina KCG-30, ϕ 2.5 × 20 cm). Brown-yellow and green bands were observed. The former was eluted with n-hexane/benzene (1/1) to give a small amount of $Ni(CO)_2(PPh_3)_2$. The latter was eluted with benzene/ethyl acetate (5/1). Evaporation of the eluant and crystallization from n-hexane/benzene gave green crystals of VIc (1.6 g, 78%). Found: C, 79.81; H, 4.02; P, 4.79. $C_{45}H_{35}PONi$ calcd.: C, 79.32; H, 5.18; P, 4.50%. Molecular weight 674 (calcd. 681).

Reaction of $(\eta^5\text{-}C_5H_5)Ni(PPh_3)\text{—}C{\equiv}CH$ (Ia) with ketene

When ketene generated by the pyrolysis of acetone was introduced in a solution of Ia (1.0 g, 2.44 mmol) in toluene (20 ml) at —70° C, a brown precipitate was observed and the solution turned from green to red-brown. After it had stood for 2 days at room temperature, the solution was evaporated under reduced pressure. The residue was dissolved in a small amount of chloroform and was submitted to chromatography on alumina. Elution with benzene/ethyl acetate (3/1) gave brown crystals of VIb (0.3 g, 27%), which were purified by recrystallization from chloroform/benzene. Found: C, 72.21; H, 5.02; $C_{27}H_{23}PONi$ calcd.: C, 71.56; H, 5.11%. Molecular weight 445 (calcd. 453).

Reaction of Ib with phenylacetyl chloride in the presence of triethylamine

A solution of phenylacetyl chloride (6 g, 39 mmol) in benzene (20 ml) was added dropwise to a solution of Ib (2 g, 4.1 mmol) and triethylamine (4 ml) in benzene (40 ml) at 0° C. The solution was stirred at room temperature for 1 day. The resulting triethylammonium chloride was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was separated by chromatography on alumina. From the eluent with benzene/ethyl acetate (5/1) was obtained green crystals of VIk (1.81 g, 73%). Found: C, 77.32; H, 5.23. $C_{39}H_{31}PONi$ calcd.: C, 77.38; H, 5.16%.

Reaction of $(\eta^5\text{-}C_5H_5)Fe(CO)_2\text{—}C{\equiv}CPh$ (IIIa) with diphenylketene

A solution of IIIa (0.6 g, 2.2 mmol) and diphenylketene (0.4 g, 2.2 mmol) in benzene (15 ml) was kept at room temperature for 1 day. After removal of the solvent, the residue was submitted to chromatography on alumina. A yellow fraction which eluted with benzene/ethyl acetate (10/1) was collected. After removal of the solvent, recrystallization from benzene/hexane gave yellow crystals of VIIIa (0.82 g, 80%). Found: C, 73.57; H, 4.27. $C_{29}H_{20}O_3Fe$ calcd.: C, 73.75; H, 4.27%. Molecular weight 478 (calcd. 472).

Reaction of IIIa with phenylacetyl chloride in the presence of triethylamine

A solution of phenylacetyl chloride (3.9 g, 25 mmol) in benzene (10 ml) was added dropwise to a solution of IIIa (0.7 g, 2.5 mmol) and triethylamine (2.5 g) in benzene (30 ml) at 0° C. The mixture was stirred at room temperature for 5 h. The resulting triethylammonium chloride was removed by filtration, and the filtrate was evaporated to dryness under reduced pressure. The residue was separated by chromatography on alumina. From the eluent with benzene/ethyl acetate (10/1) were obtained yellow crystals of IV (0.86 g, 87%). Mp. 148—149°C (lit. 148—149°C [3]).

Thermal decomposition of VIc

VIc (1 g, 1.47 mmol) placed in a 10 ml of Schlenk tube was heated at 110—120°C for 2.5 h. After cooling to room temperature, the reaction mixture was chromatographed on alumina to yield 0.26 g (56%) of $Ni(CO)_2(PPh_3)_2$, benzene/hexane (1/1) being used as an eluent. The compound was identified by comparing its infrared spectrum with that of an authentic sample.

On standing of the benzene solution of VIc at room temperature for three weeks, VIc decomposed completely to give $Ni(CO)_2(PPh_3)_2$.

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