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Reaction of Dialkyl-substituted Alkynes with Carbon Dioxide Catalyzed by Nickel(0) Complexes. Incorporation of Carbon Dioxide in Alkyne Dimers and Novel Cyclotrimerization of the Alkynes

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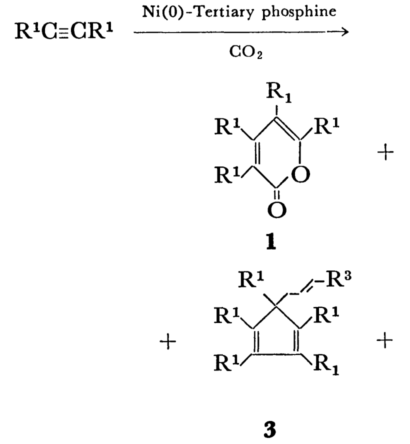
$Ni(cod)_2$–$Ph_2P(CH_2)_4PPh_2$ system (cod=1,5-cyclooctadiene) catalyzed the reaction of 3-hexyne, for example, with CO_2 to give a CO_2 incorporated product, *i.e.*, tetraethyl-2-pyrone, in a fairly good yield together with novel two cyclotrimers of the alkyne having cyclopentadiene structures, *i.e.*, pentaethyl-5-(1-propenyl)-1,3-cyclopentadiene and pentaethyl-5-allyl-1,3-cyclopentadiene. The novel two cyclotrimers were formed selectively on $Ni(cod)_2$–PPh_3 system under CO_2, whereas under N_2 the main trimer was hexaethylbenzene. A nickelacyclopentadiene intermediate has been proposed for the pyrone formation. The novel two cyclotrimers were also formed on the oligomerization catalyzed by a cationic nickel hydride complex, $[HNi(Ph_2PCH_2CH_2PPh_2)_2]OCOCF_3$, together with a novel dimer having a methylenecyclobutene structure, *i.e.*, 1,2,4-triethyl-3-ethylidenecyclobutene. The effect of phosphine added and that of active-hydrogen compounds on the novel oligomerization are mentioned.

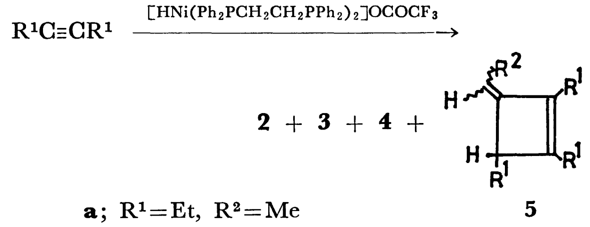
We are currently studying the CO_2 chemistry for the purpose of using it as a raw material for organic syntheses. There are many reports on the reaction of metal compounds with CO_2 in recent years but only a few examples of the catalytic fixation of CO_2 in organic compounds by transition metals have been known. Earlier papers in this series have dealt with novel reactions of CO_2 with dialkyl-substituted alkynes like 3-hexyne and 4-octyne to form pyrone derivatives (**1**) catalyzed by $Ni(cod)_2$–tertiary phosphine system.[1] This reaction is interesting because CO_2 can be catalytically linked in an alkyne dimer. In addition to the pyrone (**1**) we got two novel cyclotrimers having cyclopentadiene structures, **2** and **3**, which were accompanied by hydrogen migration together with a usual cyclotrimer, hexaalkylbenzene (**4**). Small amounts of several other products including two tetramers of the alkynes were also formed.



a; R^1=Et, R^2=Me, R^3=H
b; R^1=Pr^n, R^2=Et, R^3=Me

The course of the reaction between CO_2 and alkynes was quite sensitive to the phosphine added, resulting in significantly altered products distributions.

It has also been found that a cationic nickel hydride complex $[HNi(Ph_2PCH_2CH_2PPh_2)_2]OCOCF_3$ catalyzed the novel cyclotrimerization of alkynes to afford **2** and **3**. In this system a novel dimer (**5**) having a methylenecyclobutene structure was also formed.[2]



a; R^1=Et, R^2=Me
b; R^1=Pr^n, R^2=Et

Although cyclotrimerization of internal alkynes to benzene derivatives has been catalyzed by various kinds of nickel complexes, cyclotrimerization accompanied by hydrogen migration seems rather rare.[3]

In this paper we wish to describe the effect of phosphine added on the CO_2-alkyne reaction and that of active-hydrogen compounds on the novel oligomerization of the alkyne.

Results and Discussion

The results of the reaction between CO_2 and 3-hexyne and 4-octyne employing a variety of tertiary phosphines are summarized in Tables 1 and 2, respectively. Almost the same effects of the phosphine

TABLE 1. REACTION OF 3-HEXYNE CATALYZED BY $Ni(cod)_2$-PHOSPHINE SYSTEM UNDER CO_2 PRESSURE[a)]

Phosphine	Conversion %	Yield/%[b)]			
		1a	2a	3a	4a
$Ph_2P(CH_2)_4PPh_2$	96	57	23	2	2
	21[c)]	7	2	0.2	trace
	99[d)]	54	25	4	2
$Ph_2P(CH_2)_3PPh_2$	—[e)]	2	2	1	0.3
$Ph_2P(CH_2)_2PPh_2$	82	13	46	6	2
PPh_3	99	9	66	7	3
$Me_2P(CH_2)_2PMe_2$	71	1	4	1	trace

a) 3-Hexyne; 8.8 mmol, $Ni(cod)_2$; 0.4 mmol, $R_2P(CH_2)_nPR_2$ (R=Ph, n=4,3,2; R=Me, n=2); 0.8 mmol, PPh_3; 1.6 mmol, benzene; 5 ml, CO_2; 50 kg cm^{-2} at 25 °C: 120 °C, 20 h. b) Based on 3-hexyne charged (by GLC). c) 0.5 h. d) 0.06 mmol of water was added. e) Not analyzed.

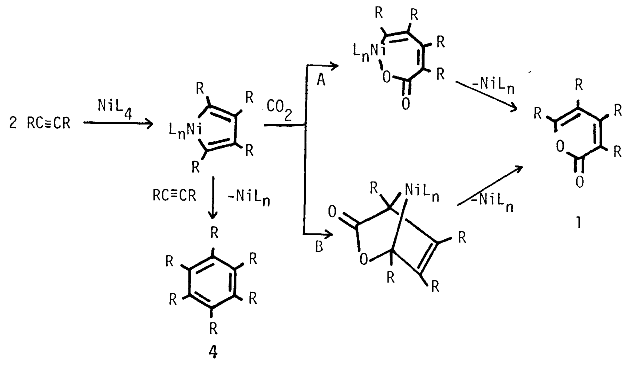
TABLE 2. REACTION OF 4-OCTYNE CATALYZED BY Ni(cod)$_2$-PHOSPHINE SYSTEM UUNDER CO$_2$ PRESSURE[a)]

Phosphine	Conversion (%)	Yield/%[b)] 1b	2b	3b	4b
$Ph_2P(CH_2)_4PPh_2$	98	60	21	3	1
$Ph_2P(CH_2)_2PPh_2$	96	12	72	6	3
	96[c)]	11	58	7	—[d)]
	56[e)]	3	23	23	3
PPh_3	100	14	75	4	4

a) 4-Octyne; 6.8 mmol, and the other conditions were the same as those in Table 1. b) Based on 4-octyne charged (by GLC). c) 0.4 mmol of water was added. d) Not analyzed. e) 6.5 mmol of water was added.

were observed in 3-hexyne and 4-octyne reactions. The ditertiary phosphine, $Ph_2P(CH_2)_4PPh_2$, was found to be the most effective for the formation of the pyrone (**1**), whereas the novel cyclotrimer (**2**) was obtained as the main product in the $Ph_2PCH_2CH_2PPh_2$ and PPh_3 systems. In case of $Ph_2P(CH_2)_3PPh_2$, 3-hexyne reacted only scarcely. In the $Me_2PCH_2CH_2PMe_2$ system, higher oligomers of 3-hexyne were the main products with a low conversion of 3-hexyne.

A possible mechanism for the pyrone formation involves a nickelacyclopentadiene as an intermediate (Scheme 1).[4)] The formation of the nickelacyclopentadiene complex from two moles of alkyne and a nickel complex is followed by CO_2 insertion into a nickel-carbon bond to give a carboxylated complex, which then eliminates the pyrone with intramolecular C–O coupling (Route A). Another route involving [4+2]cycloadditions of the cyclopentadiene complex with CO_2 in the sense of Diels-Alder reaction (Route B) cannot be eliminated but is less probable because CO_2 does not undergo [4+2]cycloaddition with dienes.[5)] Attack of another alkyne molecule to the nickelacyclopentadiene complex will result in the formation of a benzene derivative.



Scheme 1.

The diphosphines of the type $Ph_2P(CH_2)_nPPh_2$ have high coordinating ability by chelation. ^{31}P NMR studies[6)] show that the bonding ability to Ni(0) is in the order

$$Ph_2P(CH_2)_3PPh_2 \approx Ph_2P(CH_2)_2PPh_2 > Ph_2P(CH_2)_4PPh_2.$$

In case of $Ph_2P(CH_2)_3PPh_2$, the reaction took place with great difficulty. This diphosphine has such a high coordinating ability that blocks active sites of nickel to stop the reaction almost completely.

In the proposed scheme above, CO_2 is acting as an electrophile. So a nickel complex bearing more basic ligands is expected to react profitably with CO_2. But the experimental result showed that the diphosphine $Me_2PCH_2CH_2PMe_2$, which is more basic than the corresponding phenyl derivative $Ph_2PCH_2CH_2PPh_2$, was scarcely effective for the formation of the pyrone. This may be ascribed to the steric bulkiness of the phenyl groups in the latter phosphine: CO_2 is competing with an alkyne molecule in reacting with the nickelacyclopentadiene intermediate. Smaller molecule (CO_2) can preferencially react with the intermediate in the $Ph_2P(CH_2)_nPPh_2$ system.

The marked effect of the diphosphine $Ph_2P(CH_2)_4PPh_2$ on the pyrone formation can be ascribed to its adequate coordinating ability and the steric bulkiness.

The reactivity of the other internal alkynes toward CO_2 was also examined. 2-Hexyne gave possible four isomers of 2-pyrone with ill selectivity and also gave many isomers of cyclopentadiene derivatives on Ni(cod)$_2$–$Ph_2P(CH_2)_4PPh_2$ system. 2-Butyne did not react with CO_2 at 120 °C on 20 h reaction by the same (or –PPh_3) system in benzene only giving a higher oligomer in very small amount. A reaction mixture of 2-butyne after 40 h reaction at 120 °C by Ni(cod)$_2$–PPh_3 system, however, showed a carbonyl stretching vibration at 1705 cm^{-1} in its IR chart indicating that 2-butyne reacted with CO_2. But the amount of the product was too small to decide the structure. Diphenylacetylene did not react at all under these reaction conditions.

Various kinds of organometallic compounds are known to oligomerize acetylenic compounds into cyclic trimers. The product is hexasubstituted benzene in case of a disubstituted alkyne. The other type of catalytic cyclotrimerization has not been observed for disubstituted alkynes.

In the present reaction of disubstituted alkynes under CO_2, novel cyclotrimerization accompanied by hydrogen migration occurred: Ni(cod)$_2$–$Ph_2PCH_2CH_2PPh_2$ system afforded a novel trimer (**2b**) in 72% yield on the reaction of 4-octyne under CO_2 pressure as shown in Table 2. So the further investigation on the oligomerization of disubstituted alkynes was made. Results of the oligomerization of 3-hexyne and 4-octyne by nickel complexes are summarized in Table 3. The effect of CO_2 was remarkable because Ni($Ph_2PCH_2CH_2PPh_2$)$_2$ complex or Ni(cod)$_2$–$Ph_2PCH_2CH_2PPh_2$ (1:1) system scarcely catalyzed the oligomerization of 3-hexyne. Ni($Ph_2PCH_2CH_2PPh_2$)$_2$–AcOH (or –PhOH) system afforded a small amount of the cyclopentadiene derivatives. When PPh_3 was used **2a** was formed selectively under CO_2 as shown in Table 1. Under N_2, however, the main product was **4a.** Such effect of CO_2 to alter the catalyst properties has been also observed in the dimerization of butadiene catalyzed by transition metal complexes. For example, Pt(PPh_3)$_3$ converts butadiene to a cyclic dimer, 4-vinylcyclohexene, under N_2 or Ar atmosphere. However a linear dimer, 1,3,7-octatriene, becomes the

TABLE 3. OLIGOMERIZATION OF 3-HEXYNE AND 4-OCTYNE BY NICKEL CATALYSTS[a)]

Alkyne	Catalyst	Additive	Conversion	Yield/%[b)]			
			%	**2**	**3**	**4**	**5**
3-Hexyne	$Ni(Ph_2PCH_2CH_2PPh_2)_2$	—	*ca.* 0	0	0	trace	0
		AcOH	9	2	2	trace	1
		PhOH	10	3	5	trace	1
		MeOH	*ca.* 0	0	0	trace	0
	$Ni(cod)_2$-$Ph_2PCH_2CH_2PPh_2$ (1: 1)	—	5	1	0	1	0
	$Ni(cod)_2$-PPh_3 (1: 4)	—	72[c)]	9	4	39	0
	H-Ni^+	—	99[d)]	4	16	3	36
4-Octyne	H-Ni^+	—	87[d,e)]	4	9	trace	18
	H-Ni^+ [f)]	—	21[d,e)]	1	1	trace	7

a) 3-Hexyne 8.8 mmol, 4-octyne 6.8 mmol, nickel complex 0.4 mmol, additive 0.4 mmol, benzene 5 ml: 120 °C, 5 h. H-Ni^+-$[HNi(Ph_2PCH_2CH_2PPh_2)_2]OCOCF_3$. b) Based on alkyne charged(by GLC). c) 20 h. d) In these reactions considerable amounts of oily products were also formed, the IR spectra of which indicated the existence of CF_3COO- group. e) 90 °C. f) 0.08 mmol.

predominant product when CO_2 is introduced.[7)] In this case a direct effect of CO_2 on the catalyst has been suggested.

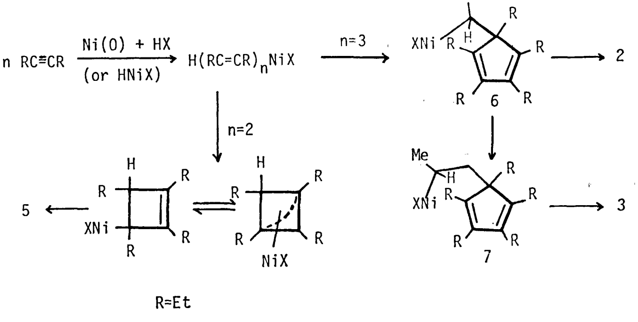
It is necessary to make a complex in a coordinately unsaturated state for the occurrence of the reaction. It has been said that a protic acid such as PhOH has an effect to liberate the ligand around the metal atom to place the complex in such a state.[8)] Even if a protic acid or CO_2 has such a function, the product will be as benzene derivative.

The intermediacy of transition metal hydride complexes in the catalytic oligomerization of olefins and diolefins accompanied by hydrogen migration has been recognized. Various nickel hydride complexes have been obtained from the reaction of zerovalent nickel with acids such as H_2SO_4, HCl, CF_3COOH, $HClO_4$, C_6H_5OH, and CH_3COOH by protonation or oxidative addition. Although the starting nickel complex is not a hydride one, carbonic acid from a catalytic amount of water and CO_2 may be a candidate for producing a nickel hydride species in the present system. Water was added to examine the effect on the product distribution in alkyne oligomerization catalyzed by $Ni(cod)_2$–$Ph_2PCH_2CH_2PPh_2$ system under CO_2. 0.15 Equivalent of water to nickel had a slight effect for the formation of **2a** and **3a** under CO_2 as shown in Table 1. The possibility that **2a** was derived from **3a** by isomerization might be excluded because with a short reaction time of 0.5 h rather than the usual 20 h, the distribution of the products did not significantly change. One or excess molar equivalent of water brought about the lowering of the catalytic activity, decreasing the selectivity for **1b** and **2b**, and increased the selectivity for **3b** as shown in Table 2. The preferencial formation of **3** over **2** resembled the results in the nickel hydride complex system (*vide infra*).

In order to clarify the role of hydride species on the alkyne oligomerization, the catalytic action of a cationic hydride complex, $[HNi(Ph_2PCH_2CH_2PPh_2)_2]$-$OCOCF_3$, which was prepared from $Ni(Ph_2PCH_2CH_2$-$PPh_2)_2$ and CF_3COOH,[9)] was examined. Actually this complex oligomerized 3-hexyne (and 4-octyne) into **2**, **3**, and **4**, and in this case a novel dimer, 1,2,4-triethyl-3-ethylidenecyclobutene (**5a**), which was not yielded in the CO_2-concerned system, was also obtained as the main product. This is a rare example of the catalytic dimerization of internal alkynes involving the migration of hydrogen. There is a possibility that the oligomerization of 3-hexyne was catalyzed by traces of acid.[10)] But it could be excluded by a control experiment. The products of these types were formed in reactions catalyzed by metallic species.

It is not certain at the present time whether CO_2 has a direct effect on the catalyst or has a tendency to produce a hydride species. But at least a certain nickel hydride complex can catalyze the novel cyclotrimerization.

Although we could not get positive data by NMR study (see the experimental part), we tentatively propose the following scheme for the novel cyclotrimerization and dimerization of 3-hexyne as a possible one by analogy with the one proposed by Maitlis on the palladium induced cyclotrimerization of alkynes.[3)] The σ-butadienyl ($n=2$) and the σ-hexatrienyl ($n=3$) complex can ring close to the cyclobutenyl and the cyclopentadiene complex which is then converted into **5** and **2**, respectively. If **6** isomerizes into another cyclopentadiene complex (**7**) with 1,2-hydride shift,[3)] **3** is formed.



Scheme 2.

Certainly other mechanisms are possible but one other possibility for the formation of the dimer **5** is mentioned here: That is the isomerization of a cyclobutadiene compound to the dimer (**5**).[11,12)]

Experimental

IR, ^1H NMR (coupled with spin decoupling method), ^{13}C NMR (coupled with off-resonance technique), mass, and UV spectra were recorded on following apparatus, respectively; Shimadzu IR-430, Hitachi R-24A (60 MHz), JNM MH-100, JMS 06H, and Shimadzu UV 200. Quantitative analyses were performed by GLC on a Shimadzu GC-3AH instrument equipped with a FFAP column with helium as a carrier gas. Preparative GLC was performed on a Shimadzu GC-2H instrument equipped with a FFAP column with hydrogen as a carrier gas.

Materials. 2-Butyne, 2- and 3-hexyne, and 4-octyne were commercially obtained. Diphenylacetylene was prepared according to the published method.[14] The diphosphines $Ph_2P(CH_2)_nPPh_2$ (n=2,3,4)[15] and $Me_2P(CH_2)_2PMe_2$[16] were synthesized according to the methods reported previously. The synthesis of the cationic nickel hydride complex $[HNi(Ph_2PCH_2CH_2PPh_2)_2]OCOCF_3$ was reported previously.[1]

Reaction of 3-Hexyne with CO_2 Catalyzed by Nickel Complexes. To a 100 ml stainless steel autoclave equipped with a magnetic agitator, benzene (5 ml), 3-hexyne (1 ml, 8.8 mmol), $Ni(cod)_2$ (110 mg, 0.4 mmol), and $Ph_2P(CH_2)_4PPh_2$ (341 mg, 0.8 mmol) were added under N_2 atmosphere. Then CO_2 was introduced to the pressure of 50 kg·cm^{-2}. The autoclave was heated to 120 °C and agitated for 20 h. The reaction mixture was analyzed by GLC. The other alkynes were reacted with CO_2 similarly.

Oligomerization of 3-Hexyne Catalyzed by the Cationic Nickel Hydride Complex. To a 20 ml glass ampoule, benzene (5 ml), 3-hexyne (1 ml, 8.8 mmol), and $[HNi(Ph_2PCH_2CH_2PPh_2)_2]OCOCF_3$ (0.387 g, 0.4 mmol) were added under N_2 atmosphere. After the ampoule was cooled in liquid N_2, it was evacuated, sealed, and then agitated for 5 h at 120 °C. The reaction products were analyzed by GLC. Oligomerization of alkynes in other systems was performed similarly.

Identification of Products. Volatile products were flash distilled from the reaction mixtures (oil bath temperature of ≈200 °C) at 1 mmHg,* and were purified by preparative GLC.

*Tetraethyl-2-pyrone (**1a**)*: IR (neat): 1700 (C=O), 1630 (C=C), and 1550 cm^{-1} (C=C). ^1H NMR (C_6D_6): δ 0.5—1.3 (12H, m, CH_3), 1.6—2.2 (6H, m, CH_2), and 2.4 (2H, q, J=5.4 Hz, CH_2). MS: m/e (rel intensity), 208 (M^+, 16), 180 (27), 165 (100), and 57 (18). UV$_{max}$ (EtOH): 304 nm.

*Tetrapropyl-2-pyrone (**1b**)*: IR (neat): 1705 (C=O), 1635 (C=C), and 1550 cm^{-1} (C=C). ^1H NMR (C_6D_6): δ 0.5—2.7 (m, CH_3 and CH_2). Found: C, 77.83; H, 11.62%. Calcd for $C_{17}H_{28}O_2$: C, 77.22; H, 10.67%.

*Pentaethyl-5-(1-propenyl)-1,3-cyclopentadiene (**2a**)*: IR (neat): 972 cm^{-1} (*trans* C=C). ^1H NMR (C_6D_6): δ 0.44 (3H, t, J=7.0 Hz, $C_{(5)}$–$CH_2C\underline{H}_3$), 0.96 (12H, m, CH_3), 1.50 (3H, d, J=6.0 Hz, $C\underline{H}_3CH$=), 1.60 (2H, q, J=7.0 Hz, $C_{(5)}$–$C\underline{H}_2CH_3$), 1.85—2.34 (8H, m, CH_2), 4.81 (1H, d, J=15.6 Hz, $\underline{H}C$=$CHCH_3$), and 5.33 (1H, m, HC=$C\underline{H}CH_3$). ^{13}C NMR (CD_3COCD_3): δ 144.9 (s), 143.0 (s), 136.2 (d), 122.1 (d) 64.2 (s), 22.9, 19.5, 19.2, 18.4, 15.6, 15.2, and 7.8. MS: m/e (rel intensity), 246 (M^+, 60), 217 (100), 189 (24), and 161 (22). UV$_{max}$ (EtOH): 206, 239, and 265 nm. Both the large spin coupling constant J=15.6 Hz in the ^1H NMR spectrum and the strong absorption at 972 cm^{-1} in the IR spectrum indicate that the double bond in the propenyl group has the *trans* configuration.

*Pentapropyl-5-(1-butenyl)-1,3-cyclopentadiene (**2b**)*: IR (neat): 970 cm^{-1} (*trans* C=C). ^1H NMR (C_6D_6): δ 0.7—1.1 (18H, m, CH_3), 1.2—1.9 (12H, m, CH_2), 1.9—2.5 (10H, m, CH_2C=), 4.81 (1H, d, J=15.4 Hz, $\underline{H}C$–CHEt), and 5.47 (1H, dt, J=15.4 and 6.5 Hz, HC=$C\underline{H}$Et). The olefinic proton at δ 5.47 ppm appeared as a doublet by irradiation of the methylene proton centered at δ 2.15 ppm. This indicates the existence of the $-CH=CHCH_2-$group. Both the large spin coupling constant J=15.4 Hz and the strong absorption at 970 cm^{-1} in the IR spectrum indicate that the double bond in the 1-butenyl group has the trans configuration.

*Pentaethyl-5-allyl-1,3-cyclopentadiene (**3a**)*: IR (neat): 1640 (C=C), 990 (C=C), and 910 cm^{-1} (C=C). ^1H NMR (C_6D_6): δ 0.37 (3H, t, J=7.0 Hz, $C_{(5)}$–$CH_2C\underline{H}_3$), 0.75—1.15 (12H, m, CH_3), 1.38 (2H, q, J=7.0 Hz, $C_{(5)}$–$C\underline{H}_2CH_3$), 1.70—2.35 (10H, m, CH_2), and 4.50—5.50 (3H, m, CH_2=CH). ^{13}C NMR (CD_3COCD_3): δ 143.4 (s), 143.1. (s), 135.9 (d), 114.7 (t), 61.6 (s), 39.9, 27.9, 19.3, 18.7, 15.5, 14.3, and 8.0.

*Pentapropyl-5-(2-butenyl)-1,3-cyclopentadiene (**3b**)*: IR (neat): 965 cm^{-1} (*trans* C=C). ^1H NMR (C_6D_6): δ 0.6—1.1 (15H, m, CH_3), 1.2—1.7 (15H, m, CH_2 and CH_3C=), 1.8—2.4 (10H, m, CH_2C=), and 4.9—5.6 (2H, m, CH=CH). The existence of the CH_3CH=C group was confirmed by a spin decoupling experiment; The methyl group which absorbed at δ 1.40 ppm as an indistinct doublet in the array of the methylene proton peaks collapsed to a singlet by irradiation of the olefinic protons. The strong absorption at 965 cm^{-1} in the IR spectrum suggests that the double bond in the 2-butenyl group has the *trans* configuration.

*1,2,4-Triethyl-3-ethylidenecyclobutene (**5a**)*: IR (neat): 800 cm^{-1} (CH=C<). ^1H NMR (CD_3COCD_3): δ 0.7—1.2 (9H, m, CH_3), 1.2—1.7 (2H, m, CH_2), 1.59 (3H, d, J=7.4 Hz, $C\underline{H}_3CH$=), 1.8—2.4 (4H, m, $CH_3C\underline{H}_2C$=), 2.72 (1H, t, J=5.7 Hz, $-\overset{|}{C}H-$), and 4.58 (1H, q, J=7.4 Hz, $CH_3C\underline{H}$=). ^{13}C NMR (CD_3COCD_3): δ 152.9 (s), 144.0 (s), 143.8 (s), 102.8 (d), 48.5 (d), 24.8, 20.7, 20.4, 14.0, 13.7, 12.6, and 11.9. UV$_{max}$ (n-hexane): 256 nm (ε 6500). We could not determine the geometry of the ethylidene moiety.

*1,2,4-Tripropyl-3-propylidenecyclobutene (**5b**)*: IR (neat): No characteristic peaks were observed other than those due to the propyl groups. ^1H NMR (C_6D_6): δ 0.5—2.5 (26H, m, CH_3 and CH_2), 2.90 (1H, t, J=5.3 Hz, $-\overset{|}{C}H-$), and 4.72 (1H, t, J=8.1 Hz, Et$\underline{H}C$=). This compound gave a very similar NMR spectrum to the ethyl counterpart (**5a**). The geometry of the exocyclic double bond could not be determined.

In these experiments it was difficult to assign the multiplicities of the methyl and methylene carbons in **2a**, **3a**, and **5a** by the off-resonance proton-decoupled technique mainly due to the overlap of the bands.

The Study of the Reaction between the Cationic Nickel Complex and 3-Hexyne by ^1H NMR. To a solution of 0.484 g (0.5 mmol) of the cationic nickel hydride complex $[HNi(Ph_2PCH_2CH_2PPh_2)_2]OCOCF_3$ in 5 ml of benzene, 113 µl (1 mmol) of 3-hexyne was added with stirring at room temperature. Orange oil was formed immediately at the bottom of the reaction vessel. So this system was unsuitable for NMR study unfortunately. Then the solvent was switched from benzene to CH_2Cl_2. To a solution of 0.1938 g (0.2 mmol) of the nickel complex in 0.5 ml of CH_2Cl_2 was added 45.4 µl (0.4 mmol) of 3-hexyne at room temperature. The homogeneous orange solution was quickly transferred into a NMR tube under N_2, then it was placed in the spectrometer of probe temperature 35 °C. The spectrum showed resonances of 3-hexyne δ 1.0 (CH_3) and 2.0 (CH_2) and

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* 1 mmHg=133.322 Pa.

those characteristic of the hydride complex, a broad triplet and a broad singlet due to the ligand at δ 2.4 and 7.1, respectively and a quintet of the hydride at δ -13.0. In 2 h the initial resonances at δ 7.1 and -13.0 disappeared almost completely and those at δ 1.0, 2.0, and 2.4 became broad with appearence of two new resonances at δ 7.5 (broad singlet) and 0.5 (triplet). During the experiment the color of the sample changed into dark red and finally into deep blue. Although GLC analysis showed the formation of **5a** in a low yield, we might not observe the exact course of the reaction because the color change did not seem normal.

References

1) Y. Inoue, Y. Itoh, and H. Hashimoto, *Chem. Lett.*, **1977**, 855; **1978**, 633.

2) Y. Inoue, Y. Itoh, and H. Hashimoto, *Chem. Lett.*, **1978**, 911.

3) There are several reports on the non-catalytic trimerization of 2-butyne to cyclopentadiene derivatives by palladium compounds: T. R. Jack, C. J. May, and J. Powell, *J. Am. Chem. Soc.*, **99**, 4707 (1977); P. M. Maitlis, *Acc. Chem. Res.*, **9**, 93 (1976), and references cited therein.

4) We tried to provide such an example by making a complex analogous to the proposed cyclopentadiene intermediate. A 2,3,4,5-tetraphenylnickelacyclopentadiene complex was synthesized by the Eisch's method[13] by reaction of $NiCl_2(PPh_3)_2$ with (*E*,*E*)-1,4-dilithio-1,2,3,4-tetraphenylbutadiene. But this complex did not react with CO_2 under the reaction conditions. This system was not adequate because diphenylacetylene did not react with CO_2 (See the text). A similar reaction of CS_2 with cobaltacyclopentadiene complexes to give 2*H*-thiopyran-2-thiones has been reported; Y. Wakatsuki and H. Yamazaki, *J. Chem. Soc., Chem. Commun.*, **1973**, 280.

5) J. Hamer and J. A. Turner, "1,4-Cycloadditions," ed by J. Hamer, Academic Press, New York (1967), p. 205.

6) C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

7) J. F. Kohnle, L. H. Slaugh, and K. L. Nakamaye, *J. Am. Chem. Soc.*, **91**, 5904 (1969).

8) Y. Iwamoto and S. Yuguchi, *Kogyo Kagaku Zasshi*, **71**, 233 (1968).

9) R. A. Schunn., *Inorg. Chem.*, **9**, 394 (1970).

10) P. E. Peterson and J. E. Duddey, *J. Am. Chem. Soc.*, **88**, 4990 (1966); **85**, 2865 (1963).

11) G. Criegee, J. Dekker, W. Engel, P. Ludwig, and K. Noll, *Chem. Ber.*, **96**, 2362 (1963).

12) E. M. Arnett and J. M. Bollinger, *J. Am. Chem. Soc.*, **86**, 4729 (1964).

13) J. J. Eisch and J. E. Galle, *J. Organomet. Chem.*, **96**, C23 (1975).

14) L. I. Smith and M. M. Falkof, *Org. Synth.*, **22**, 50 (1942).

15) W. Hewertson and H. R. Watson, *J. Chem. Soc.*, **1962**, 1490.

16) H. Niebergall and B. Langelfeld, *Chem. Ber.*, **93**, 1852 (1960).