

pA with pA was facilitated slightly by the presence of poly(U) but much less than the transamidation reaction. Poly(U) did, however, stabilize compound I against hydrolysis, presumably through the formation of a triple helix. We used a solution containing 0.0125 M [8-¹⁴C]-pA (specific activity 0.32 mCi/mmol), 0.0125 M Gly-N-pA, 0.075 M MgCl₂, 0.2 M NaCl, and 0.125 M carbodiimide. After 3 days at 0° and at pH 7.0, we obtained a 5.5% yield of compound I in the absence of imidazole or poly(U), a 9.5% yield in the presence of 0.05 M poly(U), a 23.5% yield in the presence of 0.125 M imidazole buffer, and a 43.5% yield in the presence of both poly(U) and imidazole. We believe that the carbodiimide activates the carboxyl group of Gly-N-pA and that the activated carboxyl derivative is rapidly converted to an imidazolidine. The imidazolidine then reacts selectively with the OH groups of pA.⁵

It is not clear whether the template-directed transamidation reaction has any prebiotic significance. We anticipate that compounds of the type ImpA-2'(3')-Gly will undergo template-induced polymerizations to give oligomers that could be interesting in this context.

Acknowledgment. This work was supported by NIH Grant No. GM 13435.

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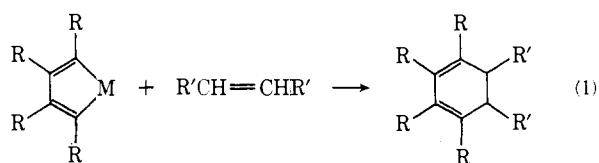
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Received January 18, 1974

Cobaltacyclopentene Complex as an Intermediate in Cobalt-Catalyzed Cooligomerization of Diphenylacetylene with Cyano Olefins

Sir:

The catalysis of the oligomerization of acetylenes, especially cyclotrimerization, by transition metal complexes has been extensively studied, but only a few examples of the cooligomerization of acetylenes with olefins have been noted.¹ The linear and cyclo trimerization of two molecules of acetylene with one molecule of olefin have been catalyzed by NiBr₂(PPh₃)₂, Ni(CO)₂(PPh₃)₂, and other nickel catalysts.² Although the reaction mechanism is not clear in these systems, some suggest one which involves metallocyclopentadiene intermediacy, as in eq 1.^{2a-e}



In the course of our studies on the cobalt-catalyzed synthesis of pyridines from acetylenes and nitriles,³ we have found that diphenylacetylene cooligomerizes with some cyano olefins. In the present communication, we

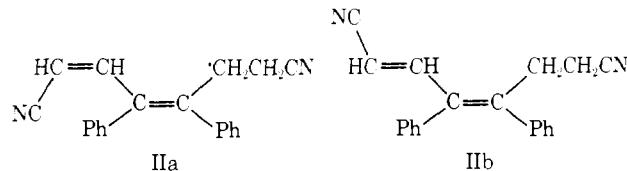
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report this new type of cooligomerization and propose a mechanism involving a novel intermediate.

The reaction of diphenylacetylene with acrylonitrile in benzene at 70° in the presence of π-C₅H₅Co(PPh₃)-(PhC≡CPh) (I) gives colorless crystals with the composition (PhC₂Ph)(CH₂CHCN)₂ (II) in 560% yield based on I. This compound is a 1:1 mixture of two isomers which were separated by chromatography on alumina: IIa, mp 126–128°; IIb, mp 101.5–102°. On the basis



of pmr spectra, the structures illustrated were assigned to these compounds.

When π-C₅H₅Co(PPh₃)(PhC≡CCO₂Me) (III) is used instead of I, the catalytic reaction does not proceed, probably owing to the formation of stable intermediates; indeed the reaction of III with acrylonitrile at room temperature affords stable diene complex IV, 155–157° dec, in 16% yield.

The reaction of III with dimethyl maleate in benzene at room temperature gives a 30% yield of red crystalline complex V, 177–178° dec, isolated by chromatography and purified by crystallization from dichloromethane-hexane. The structure of this compound has been established by a single-crystal X-ray analysis. Crystal data are: *a* = 12.330, *b* = 17.834, *c* = 8.955 Å; α = 98.12, β = 116.13, γ = 81.13°; *V* = 1741 Å³; *d*_{meas} = 1.36, *d*_{calcd} = 1.359 g/cm³ (assuming 0.25 mol of CH₂Cl₂ per mole of complex) for *Z* = 2; space group *P*1. The structure determination was based on 4673 independent reflections, collected on a Rigaku four-circle automatic diffractometer using Cu K α radiation monochromated from graphite. The block diagonal least-squares refinement converged to a conventional *R* value of 10.6%. The molecule consists of a cyclopentadienyl group, triphenylphosphine, and cobaltacyclopentene ring (Figure 1). The cobalt atom and C(1), C(2), and C(3) are in a same plane with C(4) bent from this plane by 34.2°.

The formation of metallocycles is an important feature of this type of acetylene complex; the reactions of I with acetylenes,⁴ carbon disulfide, and carbonyl sulfide⁵ have been known to yield respective five-membered metallocyclic complexes. Complex V cannot be obtained by the reaction of π-C₅H₅Co(PPh₃)(MeO₂CCH=CHCO₂Me) with PhC≡CCO₂Me.

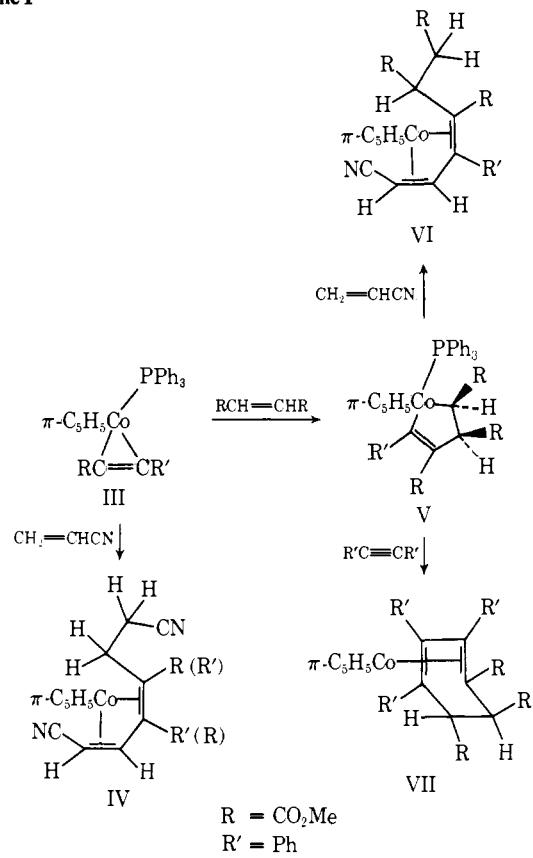
The treatment of complex V with acrylonitrile (70°) or diphenylacetylene (room temperature) in benzene affords red crystalline diene complexes VI and VII (Scheme I) in 17 and 46% yield, respectively.

These model reactions imply the mechanism shown in Scheme II for the catalytic cooligomerization reaction. The primary step of the proposed mechanism is the formation of the cobaltacyclopentene complex analogous to V. The second step is the displacement of triphenylphosphine by acrylonitrile followed by the transfer

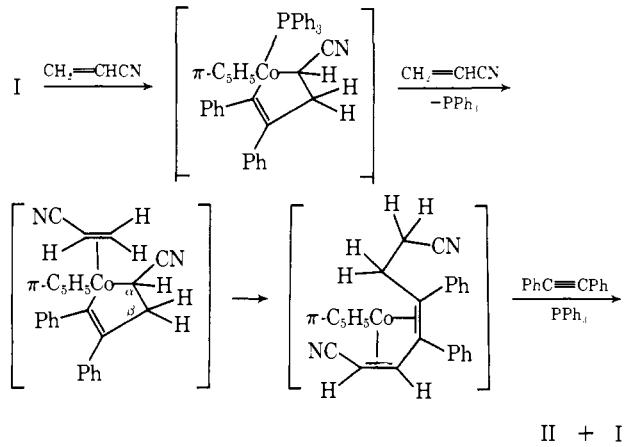
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Scheme I



Scheme II



of hydrogen⁶ affording the diene complex intermediate analogous to **IV** or **VI**.

In contrast, the reaction of diphenylacetylene with methacrylonitrile produces a compound formulated as $(\text{PhC}_2\text{Ph})_2(\text{CH}_2\text{C}(\text{Me})\text{CN})$ (**VIII**), mp 190–191°, in 320% yield based on **I**.⁷ The ir and pmr spectral data of **VIII** are best accommodated by the structure shown in the figure, in which one of the methyl protons of the methacrylonitrile molecule has transferred to the diphenylacetylene carbon.

Compound **VIII** is presumably formed also via the

(6) Hydrogen may transfer either from the attacking acrylonitrile to the cobaltacyclopentene α -carbon or from the β -carbon of the cobaltacyclopentene ring to the attacking acrylonitrile. Taking into account the model reaction **V** → **VI**, the authors prefer the former case.

(7) In these cooligomerization reactions, a considerable amount of cyclobutadiene complex, $\pi\text{-C}_5\text{H}_5\text{Co}(\text{PhCCPh})_2$, is obtained, which may be formed readily on heating **X**.⁴ Therefore, the formation of **X** from **I** and diphenylacetylene is supposed to be a main reason for rather poor catalytic activity of **I**.

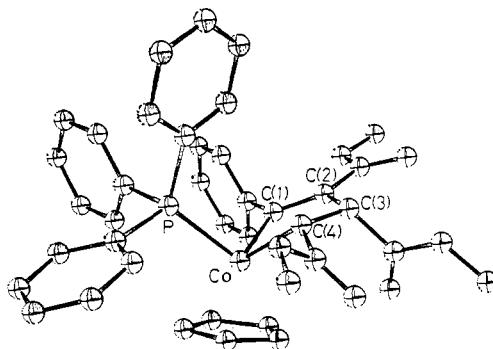
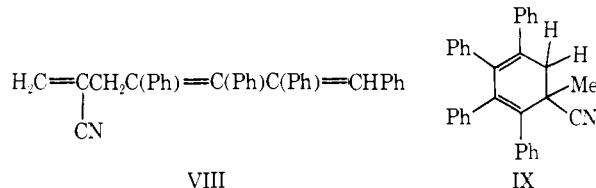


Figure 1. The molecular geometry of $\pi\text{-C}_5\text{H}_5\text{Co}(\text{PPh}_3)[(\text{PhC}_2\text{CO}_2\text{Me})(\text{MeO}_2\text{CH})_2]$ (**V**).

cobaltacyclopentene intermediate which is successively attacked by diphenylacetylene. If no transfer of hydrogen occurred, this reaction is expected to produce a cyclohexadiene derivative (**IX**) according to the model



reaction **V** → **VII**, but actually one of the methyl hydrogens transfers to the attacking diphenylacetylene molecule thus forming the straight-chain product. The alternative mechanism, i.e., attack by methacrylonitrile upon the cobaltacyclopentadiene intermediate followed by hydrogen transfer has been excluded since the treatment of cobaltatetraphenylcyclopentadiene complex,

$\pi\text{-C}_5\text{H}_5\text{Co} \cdot \text{C}(\text{Ph})=\text{C}(\text{Ph}) \cdot \text{C}(\text{Ph})=\text{C}(\text{Ph})(\text{PPh}_3)$ (**X**), with methacrylonitrile, gave only **IX** (10%) and 1,2,3,4-tetraphenyl-5- α -methylvinylpyridine (19%) as organic products, and hence no hydrogen transfer was observed.

Thus it is obvious that the relative coordination abilities between the acetylene and the olefins govern the reaction paths and consequently determine the products.

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Received March 18, 1974

Variations in Molecular Geometry along the Isoelectronic Series $\text{Co}_2(\text{CO})_8$, $[\text{FeCo}(\text{CO})_8]^-$, and $[\text{Fe}_2(\text{CO})_8]^{2-}$

Sir:

$\text{Co}_2(\text{CO})_8$ is an example of a compound whose solid state and solution structures are different. While X-ray studies¹ have indicated a C_{2v} , double CO-bridged structure (**I**) in the crystal, infrared studies² have shown that in solution the molecule exists as an equilibrium mixture of (**I**) and the nonbridged D_{3d} isomer (**II**). We wish to report that interesting changes occur in the geometry of this species as its charge is systematically varied (i.e., as each Co atom is replaced by Fe⁺).

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