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Activation of Alkynes by the Dinitrogen Complex $[CoH(N_2)(PPh_3)_3]$ Towards Catalytic Oligomerization and Cyclization Reactions

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The complex $[CoH(N_2)(PPh_3)_3]$ catalyses oligomerization and cyclization reactions of alkynes under mild conditions. Hence, alkyne cocyclotrimerization to benzene derivatives was mainly observed for ethyl propiolate, affording the three possible isomers of tricarbethoxybenzene; phenylacetylene undergoes mainly linear dimerization to *trans-Ph*C≡CCH=CH*Ph* and trimerization; linear dimers are also the predominant products from 3-hexyne, but 1-octyne (with a long chain) undergoes mainly isomerization to 2-octyne; higher oligomers are also usually formed. Except for ethyl propiolate, hydrogenated dimers are detected in low yields (e.g. *trans,trans-Ph*CH=CHCH=CH*Ph* from phenylacetylene), whereas 3-hexene is formed in considerable yield from 3-hexyne. A novel type of cocyclization reaction with a nitrile (NC*Me*) appears to occur with phenylacetylene to give (although in low yield) 4,6-dimethyl-5-phenyl-pyrimidine. Alkynols are unreactive under the chosen conditions.

(Keywords: Alkynes; Catalysis; Dinitrogen complex; Nitriles; Pyrimidine)

Die Aktivierung von Alkinen mit dem Distickstoffkomplex $[CoH(N_2)(PPh_3)_3]$ *gegenüber katalytischer Oligomerisierung und Cyclisierungsreaktionen*

Der Komplex $[CoH(N_2)(PPh_3)_3]$ katalysiert Oligomerisations- und Cyclisierungsreaktionen von Alkinen unter milden Bedingungen. Die Cyclotrimerisierung von Propinsäureethylester ergibt die drei möglichen Isomeren von Tricarbethoxybenzol; Phenylacetylen reagiert hauptsächlich zu linearen Dimeren (vor allem *trans-Ph*C≡CCH=CH*Ph*) und Trimeren; lineare Dimere herrschen auch bei 3-Hexin vor, während 1-Octin (mit langer Alkylkette) vorwiegend zu 2-Octin isomerisiert wird. In allen Fällen werden ebenfalls höhere Oligomere gebildet. Außer bei Propinsäureethylester entstehen ebenfalls in geringer Menge hydrierte Dimere (z. B. *trans,trans-Ph*CH=CHCH=CH*Ph* aus Phenylacetylen). Eine neue Art von Cocyclisierungsreaktion mit einem Nitril

(NC*Me*) scheint bei der Bildung (in geringer Ausbeute) von 4,6-Dimethyl-5-phenyl-pyrimidin aus Phenylacetylen vorzuliegen. Alkinole reagieren unter den Versuchsbedingungen nicht.

Introduction

Although alkynes and nitriles are isoelectronic with dinitrogen and also substrates of nitrogenase [1], the N_2-reducing molybdoenzyme, and in spite of their increasingly recognized value as versatile reagents [2, 3], the study of their chemistry at N_2-binding metal sites has not yet been developed [4]. Moreover, in view of the usual facile displacement of N_2, dinitrogen complexes are expected to behave as catalyst precursors. Nevertheless, only a very limited number of catalytic applications of N_2 complexes has been reported and they usually involve olefin hydrogenation, isomerization, or polymerization reactions [5], although rare examples of alkyne activation have been cited, e.g., the cyclotrimerization of disubstituted acetylenes (such as dimethyl acetylenedicarboxylate) at 110 °C to substituted benzenes catalysed by $[IrCl(N_2)(PPh_3)_2]$ [6].

Hence, a systematic study of the activation of alkynes by N_2-binding centres was initiated and, by reacting *trans*-$[ReCl(N_2)(dppe)_2]$ [*dppe* = bis(diphenylphosphino)ethane] with terminal alkynes ($HC{\equiv}CR$) or with 1-phenyl-1-propyne, a 1,2- or 1,3-hydrogen shift occurred, leading to the stable vinylidene or allene complexes *trans*-$[ReCl(C{=}CHR)(dppe)_2]$ [7] or *trans*-$[\overbrace{ReCl(\eta^2{-}CH_2{-}C{=}CHPh)}(dppe)_2]$ [8], respectively. Alkynols were decarbonylated to give carbonyl complexes [9].

However, the robust rhenium metal centre, presenting strong chelating diphosphines and the Cl π-donor with a stabilizing effect on the *trans* alkyne-derived ligand, did not show any catalytic activity.

For the present study, we have selected a dinitrogen complex with labile co-ligands, $[CoH(N_2)(PPh_3)_3]$, which is a known [10, 11] catalyst precursor for various olefin reactions, and we report our results on the catalytic activation of alkynes by this species.

Results and Discussion

The reactions of $[CoH(N_2)(PPh_3)_3]$ with alkynes were performed in the presence of a nitrile (NC*Me*) als solvent, at ambient temperature (ca. 22 °C), in order to test the possibility of the synthesis of organonitrogenated products under mild conditions. In a typical experiment (for details see Exp.), the dinitrogen complex was dissolved in acetonitrile and, upon replacement of N_2 by NC*Me* [12], an excess of the alkyne (12 : 1) was added. The solution was left stirring at 22 °C, and the organic products were separated and identified by GC-MS analyses,

Table 1. *Organic products of the reactions of alkynes with* $[CoH(N_2)(PPh_3)_3]$ *in acetonitrile*[a]

Alkyne	Products
$HC\equiv CCO_2R$ (R = Et)	*Aromatics* (74%): tricarbethoxybenzene (1,2,3-, 1,3,5- and 1,2,4-isomers)[b] Linear trimers (12%) and tetramers (13%)
$HC\equiv CPh$	*Linear dimers* (mainly *trans-Ph*$C\equiv CCH=CHPh$, 41%), *trimers* (38%) and higher oligomers (15%) Hydrogenated dimers (mainly *trans,trans-Ph*$CH=CHCH=CHPh$) (4 ~ 5%) Pyrimidine derivative: 4,6-dimethyl-5-phenyl-pyrimidine (ca. 1%)
$HC\equiv CC_6H_{13}$[c]	*2-Octyne* (34%) Linear dimers (18%) Linear hydrogenated dimers (dienes) (4%) Aromatics (ca. 1%)
$C_2H_5C\equiv CC_2H_5$	*Linear dimers* (50%) 3-Hexene (20%) Hydrogenated dimers (5%) Other products (e.g., trimers and tetramers)[d] (25%)
$HC\equiv CCH_2OH$[e] $HOCH_2C\equiv CCH_2OH$[e] $PhC\equiv CCH_3$[e]	

[a] Reactions carried out at ca. 22 °C for ca. 23 h with the initial alkyne: Co molar ratio of 12 : 1. Quoted yields relative to the initial alkyne. The main products are in italics

[b] The three isomers were obtained in similar amounts

[c] Unreacted 1-octyne was also detected (ca. 43%)

[d] Not fully identified

[e] Organic products were *not* detected

^{1}H-NMR and IR spectroscopy. A catalytic quantitative conversion of the alkyne into other organic species was observed in most cases (see Table 1).

Within the range of the tested alkynes, ethyl propiolate appeared to be the most reactive, affording as the main products (74% yield) the products of cyclotrimerization, the three possible isomers of tricarbethoxybenzene (1,2,3-, 1,3,5-, and 1,2,4-isomers) in about equal amounts together with the products of linear oligomerization, trimers and tetramers, in lower yields (12 and 13%, respectively).

Aromatic products were not obtained in considerable yield from any of the other alkynes which afforded linear dimers (in high yields) and trimers. Isomerization and hydrogeneration were also observed.

Hence, phenylacetylene gave predominantly *trans*-1,4-diphenyl-3-buten-1-yne (41%) and linear trimers (38%), whereas the linear dimeric species were the main products from the reaction of 3-hexyne (50%). Linear dimers were also formed in considerable yield (18%) from 1-octyne which, however, underwent isomerization to 2-octyne (34%) as the main product.

Hydrogenated products are formed in low yields from phenylacetylene and 1-octyne, but in greater amounts from the internal alkyne 3-hexyne which gave 3-hexene (20%) and hydrogenated dimers (5%). Although the source of hydrogen in these reactions has not been ascertained, the hydride and the phosphine ligands are plausible candidates. The cobalt metal site is known to undergo reversible *ortho*-metalation which accounts, e.g., for the hydrogen exchange of the *ortho* protons of the phenyl rings of the phosphines [13]; moreover, the involvement of phenyl protons of these ligands has also been suggested [11] to occur in some alkene reactions catalysed by this metal centre.

Ethyl propiolate, phenylacetylene and 3-hexyne were fully converted into other organic species, while 1-octyne with a long alkyl chain showed lower reactivity (only 57% conversion under identical reaction conditions) towards dimerization and oligomerization (isomerization was the main reaction) which, in part, may reflect a considerable steric requirement of the former type of reactions.

A strong dependence of the type of alkyne reactivity on the substituent is a common observation in a variety of systems, e.g., with $[Ni(CO)_2(PPh_3)_3]$ which at higher temperatures catalyses the cyclotrimerization (to aromatic species) of monosubstituted alkynes with smaller alkyl chains while those with longer chains undergo linear oligomerization [14]; the higher reactivity of propiolates was also observed in this case.

In our system, somewhat surprisingly, no organic product was detected from 1-phenyl-1-propyne and from the alkynols (propargyl alcohol, $HC{\equiv}CCH_2OH$, and 2-butyne-1,4-diol, $HOCH_2C{\equiv}CCH_2OH$). The possibility of the formation of stable alkyne complexes or of derived compounds (e.g., of the type of the above mentioned allene or carbonyl species with the $\{ReCl(dppe)_2\}$ centre) may hinder the catalytic activity of the cobalt site.

The types of alkyne reactions cited above for our cobalt centre are known to occur, although generally at higher temperatures, at various metal sites, and mechanisms have been proposed [2].

However, in the present study a nitrogenated compound, probably 4,6-dimethyl-5-phenyl-pyrimidine, appeared to be formed (although in very low yield, ca. 1%) from a curious cocyclization of phenylacetylene with two molecules of acetonitrile. In the pyrimidine product the two methyl groups are equivalent in the ^{1}H-NMR spectrum ($\delta = 2.60$ ppm in CCl_4); the chemical shift is distinct from the one of the other possible symmetrical isomer, 4,6-dimethyl-2-phenyl-pyrimidine, which could not be detected. To our knowledge this seems to correspond to a novel type of alkyne reaction which is different from the known one-step cocyclization of alkynes and nitriles catalysed by a organocobalt species (typically with a η^5-cyclopentadienyl or η^3-allyl ligand) to form 2-substituted pyridines [15], or by cobalt atoms (formed by metal evaporation and co-condensation) [16].

2-Substituted pyridines were *not* detected in this work, in agreement with the known [15] catalytic activity depressing effect of ligands such as phosphines, carbon monoxide, or isocyanides, as a result of their competition with the substrate for the metal site. Indeed, adding an equimolar amount of ethyl isocyanoacetate to the catalyst depresses completely any catalytic activity.

The formation of a 2-substituted pyridine from the cocyclization of an alkyne (two molecules) with a nitrile (one molecule) involves a metallacyclopentadiene species which is also a key intermediate in other cyclization reactions of alkynes [2, 15]. However, such a type of complex is probably not implicated in the mechanism of the generation of the pyrimidine in a reaction with a different stoichiometry (alkyne : nitrile = 1 : 2). Moreover, the formation of both the pyrimidine from *Ph*C≡CH, and 1,2,3-tricarbethoxybenzene from HC≡CCO_2*Et*, appears to involve the complete cleavage of an alkyne C≡C bond; for these reactions a carbyne-type intermediate is an appealing postulate, although no products of alkyne metathesis (e.g. diphenylacetylene from phenylacetylene) have been detected. Cocyclization reactions of alkynes with other organic species may also occur via η^2-vinyl intermediates, formed by a nucleophilic attack at an alkyne ligand [17], but the examples so far reported do not involve cleavage of a C≡C bond.

Conclusion

Although the detailed mechanisms of the reactions reported herein are unknown and a low chemo- and regioselectivity is observed for the conversion of the alkynes into other organic species, this study demonstrates the catalytic activation of alkynes under mild conditions by a well-defined dinitrogen complex of cobalt (or a derivative) and the possibility

to extend the metal promoted alkyne/nitrile reactions to the synthesis of heterocycles other than pyridine derivatives.

Experimental

^{1}H-NMR spectra were measured with a Jeol JNM PMX 60 spectrometer. GC-MS experiments have been performed with a Carlo Erba 4160 chromatograph equipped with a ChromPak SIL 5 column, and a Varian MAT 112 S apparatus.

All the reactions were carried out under identical conditions. Details are given for phenylacetylene as a typical example. The results for various alkynes are summarized in Table 1.

A solution of $[CoH(N_2)(PPh_3)_3]$ (2.19 g, 2.50 mmol) in acetonitrile (25 ml) was stirred under nitrogen for 1 h at 22 °C. A solution of phenylacetylene (3.06 g, 30 mmol) in 5 ml of acetonitrile was added dropwise. An exothermic reaction with darkening of the solution occurred. The mixture was left stirring for 23 h. After removing the solvent under vacuum from the resulting yellowish-green solution, hexane (50 ml) was added and the mixture filtered through a Florisil packed column of ca. 5 cm height. The effluent (eluted further with hexane/dichloromethane 1 : 1) was concentrated under vacuum and analyzed by GC-MS. The first fraction (eluted with hexane) consisted mainly of the linear dimers and contained also the pyrimidine, whereas the following fractions were increasingly rich in higher oligomers. Complete evaporation of the solvent and extraction of the residue with methanol separates the products of higher molecular weight (insoluble in methanol) from the other organic products.

Performing the reaction at 60 °C leads to rapid decomposition and deactivation of the catalyst, leading to only low conversion of the phenylacetylene (ca. 30%) and to the formation of higher oligomers exclusively.

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