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π-METHYLENECYCLOPROPANEBIS(TRIPHENYLPHOSPHINE)NICKEL

L.S. ISAEVA *, T.A. PEGANOVA, P.V. PETROVSKII

Nesmeyanov Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilov St., 28, Moscow V-334 (U.S.S.R.)

D.B. FURMAN, S.V. ZOTOVA, A.V. KUDRYASHEV and O.V. BRAGIN

Zelinsky Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R. Leninsky Prospect, 47, Moscow V-334 (U.S.S.R.)

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Summary

Two methods for preparing π-methylenecyclopropanebis(triphenylphosphine)-nickel are described: (1) the substitution of the ethylene ligand in π-ethylenebis(triphenylphosphine)nickel by methylenecyclopropane; (2) the interaction of Ni(acac)$_2$ with diethylaluminium ethoxide in the presence of methylenecyclopropane and triphenylphosphine.

The reactivity, some catalytic properties and the NMR (^{1}H and ^{31}P–{^{1}H}) spectra of the nickel-olefin complex obtained have been studied.

Introduction

According to the literature, the main influence on the preferential direction of catalytic conversion (di-, tri- or oligomerization) of methylenecyclopropane in the presence of nickel complexes is exerted by the nature of the ligands or the modifying additives [1–4]. Thus, dicycloocta-1,5-dienenickel alone [1], or in the presence of esters of unsaturated acids [2], induces cyclodimerization of methylenecyclopropane. With triorganophosphine-modified nickel(0) complexes [3] or with compounds of the type Ni(PR$_3$)$_n$ (R = Et, $n = 4$; Ph, $n = 4$; cyclo-C$_6$H$_{11}$, $n = 3$ etc.), methylenecyclopropane affords mainly linear and cyclic trimers.

No intermediate methylenecyclopropane nickel complexes have been isolated in these reactions, and the present paper is concerned with the synthesis and investigation of the reactivity and some catalytic properties of the zero-valent nickel complex containing methylenecyclopropane and triphenylphosphine ligands.

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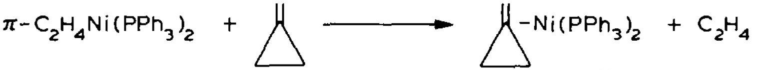
Results and discussion

The nickel complex I has been synthesised by replacement of the coordinated ethylene in π-ethylenebis(triphenylphosphine)nickel by the action of an excess of methylenecyclopropane on π-$C_2H_4Ni(PPh_3)_2$ in benzene solution. This results in the evolution of ethylene and the formation of π-methylenecyclopropanebis(triphenylphosphine)nickel (80%):



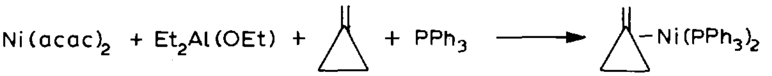
(1)

(I)

At room temperature the reaction proceeds to completion in 2 h.

The new complex I is a yellow crystalline substance, which is sensitive to atmospheric oxygen, poorly soluble in ether and petroleum ether, and more soluble in aromatic hydrocarbons. The ^1H NMR spectrum of this compound, recorded in C_6D_6, contains three singlet signals (ppm): δ 2.52 (CH_2=), 1.15 ($\Delta\nu$ 5.8 Hz) and 0.65 ($\Delta\nu$ 8.4 Hz) (CH_2<) ($J \leqslant 2.9$ Hz) (which, we believe, belong to the protons of methylenecyclopropane ligand), together with the multiplet for the phenyl ring protons of the PPh_3 ligands, at δ 7.61 (*o*-Ph) and 7.05 (*m*-, *p*-Ph) ppm. The ratio of integrated intensities of these signals is 2/2/2/12/18, which corresponds with the proposed structure for I. In the ^{31}P-{^1H} NMR spectrum of the complex I, recorded in toluene at −70°C, a quadruplet is observed which is typical of an AB system (δ_A 31.85, δ_B 32.85 ppm, J_{AB} 32 Hz). This is indicative of non-equivalence of the phosphorus atoms and, therefore, of the arrangement of the C=C bond in the P–Ni–P plane.

π-Methylenecyclopropanebis(triphenylphosphine)nickel was also prepared by an alternative method which involves the interaction of nickel acetylacetonate with diethylaluminium ethoxide in the presence of methylenecyclopropane and triphenylphosphine:



(2)

(I)

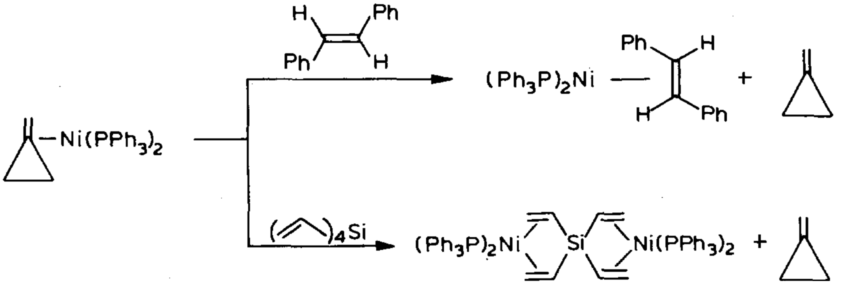
This reaction, in the same way as (1), proceeds at room temperature, but the precipitation of the yellow crystalline solid is observed only after 4 h.

The yield of I is 44%. However, for reaction (2) to be carried out successfully more highly concentrated benzene solutions of methylenecyclopropane ($\geqslant$ 1.70 *M*) must be used. Brief mention has been made of the preparation of a similar nickel complex stabilized by tri-*o*-biphenylylphosphite [5].

The nature of the methylenecyclopropane–Ni bond in the complex I was investigated independently by chemical methods. The interaction of I with olefins such as *trans*-stilbene or tetravinylsilane leads to displacement of the coordinated methylenecyclopropane and formation of π-*trans*-stilbenebis(triphenylphosphine)nickel (80%) (reaction 3) or (π-tetravinylsilane)tetrakis(triphenylphosphine)dinickel (reaction 4) (75%).

The presence of free methylenecyclopropane in the solution was shown by GLC.

A study of the catalytic conversions which methylenecyclopropane undergoes



(3)

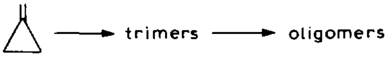
(4)

under the influence of the complex I led to observation of some significant features of these processes.

In solutions of methylenecyclopropane (MCP) in benzene, even more dilute than used in another study [4], the compound I shows appreciably higher catalytic activity (mol MCP/h × g-atom Ni) than $Ni(COD)_2/PPh_3$ (Table 1, 3): 1-(1-methyleneprop-2-enyl)-1-(2-ethylprop-2-enyl)cyclopropane (II) and 1-(2-methylenebut-3-enyl)-1-(1-ethylvinyl)cyclopropane (III) were found among the reaction products.

Methylenecyclopropane undergoes mainly trimerization in the presence of I in benzene solution as with the other catalyst [4]; however, in contrast to that study, [4] the yield of dimers reaches 17% and the oligomer content in the reaction mixture does not exceed 5% after 5 h.

It should be noted that when the conversion of methylenecyclopropane reaches 60% the oligomer yield increases about 4 times, with simultaneous decrease of the trimer content in the reaction mixture. This fact suggests that oligomers are secondary products, formed in the sequence:



For an examination of complex I, used as catalyst, we studied the behaviour of I under the conditions of the reaction (1) but over a longer period of time (24–48 h). In this case the gradual disappearance of the yellow crystalline solid first formed takes place, and the solution becomes dark red. Evaporating the reaction mixture gives a brown product (IV). The same result was obtained in the reaction of the complex I with a benzene solution of methylenecyclopropane. The treatment of IV with an excess of *trans*-stilbene leads to the formation of π-*trans*-stilbenebis(triphenylphosphine)nickel (56%) and a mixture of methylenecyclopropane trimers, in which II and III are the main components. Therefore, it may be assumed that the product IV is the mixture of nickelacycloalkanes responsible for the formation of methylenecyclopropane trimers [4].

It is very important to note that IV reacts with an excess of methylenecyclopropane again giving the complex I (52%) and the mixture of trimers II and III.

These data suggest that the process of methylenecyclopropane trimerization, in the presence of I, follows the sequence:

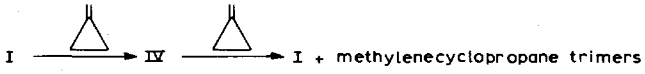
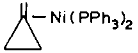
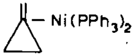


TABLE 1

DI-AND TRI-MERIZATION OF METHYLENECYCLOPROPANE (MCP) IN THE PRESENCE OF $Ni(COD)_2/PPh_3$ AND π-METHYLENECYCLOPROPANEBIS(TRIPHENYLPHOSPHINE)NICKEL

No.	Catalyst	P/Ni (mol)	[methylene-cyclo-propane] (mmol/ml)	Time (h)	Activity (mol MCP/ h g-atom Ni)	Conver-sion (%)	Selectivity (%)		
							Dimers	Trimers	Oligomers
1	$Ni(COD)_2/PPh_3$ [a]	1	8.4	8	18	84	13	42	45
2	$Ni(COD)_2/PPh_3$ [a]	2	7.6	10	12	98	3	41	56
3	 [b]	2	1.5	5	44	43	17	78	5
4	 [b]	2	1.5	18	18	62	13	68	19

[a] Ref. 4; [b] Present work.

Experimental

The ^1H NMR spectra were recorded with a Bruker WP-200SY spectrometer at 22°C. Deuterobenzene was used as a solvent for all the samples. The chemical shifts are given with respect to residual benzene (7.24 ppm). The ^{31}P-$\{^1H\}$ NMR spectra were measured on a Bruker HX-90 (with 85% H_3PO_4 as an external standard).

GLC analysis was performed on a LHM–8MD chromatograph, equipped with a flame-ionizing detector, using a 50 m × 0.25 mm column, with (dibuthyrate triethyleneglycol as filler and hydrogen as carrier gas) for identification of methylenecyclopropane. The reaction mixtures were analysed on a 1.5 m × 3 mm column (5% SE/chezasorb AW-HMDS as filler and helium as carrier gas) with the programming of temperature, ranging from 40 to 200°C.

π–Ethylenebis(triphenylphosphine)nickel was prepared according to a reported method [6].

All the experiments were carried out under an argon atmosphere using absolute solvents which were distilled under argon prior to use.

1. π-Methylenecyclopropanebis(triphenylphosphine)nickel (complex I)

(a) A benzene solution of methylenecyclopropane (26.24 mmol) was added to π-$C_2H_4Ni(PPh_3)_2$ (6.56 mmol) at 20°C. The reaction mixture was stirred for 2 h. The yellow precipitate which formed was filtered off, washed consecutively with benzene and ether, dried in vacuum to give π-methylenecyclopropanebis(triphenylphosphine)nickel 3.39 g (81%), m.p. 129–130°C (dec) (from benzene-ether). (Found: C, 74.94; H, 5.71. $C_{40}H_{38}NiP_2$ calcd.: C, 75.38; H, 5.69%).

(b) A solution of $Et_2Al(OEt)$ (15.00) mmol in ether was carefully added to an ether solution of $Ni(acac)_2$ 5.00 mmol, PPh_3 (10.00 mmol) and methylenecyclopropane (20.00 mmol) in benzene (12 ml) cooled to −20°C. The reaction mixture was stirred at 20°C for 9 h. The yellow crystalline precipitate was filtered off, washed with ether, and dried in vacuum to give 1.40 g (44%) of complex I.

(c) A solution of methylenecyclopropane (9.60 mmol) in benzene was added to product IV (1.37 mmol) at 20°C. At once, a yellow substance precipitated. After being stirred for 2 h the solid was filtered off washed with ether and dried in vacuum to give 0.45 g (52%) of complex I.

2. Product IV

(a) A benzene solution of methylenecyclopropane (23.49 mmol) was added to π-$C_2H_4Ni(PPh_3)_2$ (5.87 mmol) in benzene. The reaction mixture was stirred at 20°C for 28 h, then evaporated to dryness and the residue was dissolved in ether and treated with pentane. The brown precipitate which formed was filtered off, washed with pentane and dried in vacuum to give product IV 1.74 g (40%) (Found: C, 75.81; H, 6.49. $C_{48}H_{48}NiP_2$ calcd.: C, 77.33; H, 6.49%).

(b) A benzene solution of methylenecyclopropane (11.48 mmol) was added to a suspension of complex I (2.87 mmol) in benzene. The reaction mixture was stirred for 20 h at 20°C. After treatment of the reaction mixture as in the previous experiment product IV 0.82 g (38%) was obtained.

3. π-trans-Stilbenebis(triphenylphosphine)nickel

(a) A benzene solution of *trans*-stilbene (5.88 mmol) was added to a suspension of complex I (1.96 mmol) and the reaction mixture was stirred at 20°C for 22 h. Free methylenecyclopropane and negligible amounts of methylenecyclopropane trimers were detected in the mixture by GLC. The reaction mixture was then evaporated to minimal volume and treated with ether. The red crystalline solid which precipitated was filtered off, washed with ether and dried in vacuum to give *π-trans*-stilbenebis(triphenylphosphine)nickel 1.20 g (80%), ^{1}H NMR spectrum (C_6D_6); δ 4.01 (CH, J(H–P) ≈ 3.18; J(H–P) ≈ 1.28 Hz); 6.69–7.31 (m, C_6H_5) ppm.

(b) *π-trans*-Stilbenebis(triphenylphosphine)nickel 0.88 g (56%) was obtained from the product IV (2.15 mmol) and *trans*-stilbene 6.46 mmol under conditions of the previous experiment. According to GLC data the reaction mixture contains II and III in a ratio ~ 1 : 1.

4. *(π-Tetravinylsilane)tetrakis(triphenylphosphine)dinickel*

A benzene solution of tetravinylsilane (29.35 mmol) was added to a suspension of complex I (2.04 mmol) in benzene at 20°C. After 1 h the reaction mixture was evaporated to dryness, the residue was dissolved in ether and treated with pentane to give (π-tetravinylsilane)tetrakis(triphenylphosphine)dinickel 1.05 g (75%). The ^{1}H NMR spectrum of this compound, recorded in C_6D_6, was identical to that of known sample [7]. According to GLC analysis the solvent distilled off contained only methylenecyclopropane.

References

1 P. Binger, Angew. Chem. Int. Ed., 11 (1972) 302.
2 P. Binger, Synthesis, (1973) 427.
3 P. Binger and J. McMeeking, Angew. Chem. Int. Ed. Engl., 12 (1973) 995.
4 P. Binger, A. Brinkmann and J. McMeeking, Liebigs. Ann. Chem., (1977) 1065.
5 M. Englert, P.W. Jolly and G. Wilke, Angew. Chem. Int. Ed. Engl., 10 (1971) 77.
6 J. Ashley-Smith, M. Green and F.G.A. Stone, J. Chem. Soc. A, (1969) 3019.
7 F.F. Kayumov, L.S. Isaeva, T.A. Peganova, F.G. Yusupova, L.M. Khalilov and Yu.B. Monakov, 6th Internat. Symposium on Organosilicon Chemistry, Budapest, 1981, p. 198; J. Organomet. Chem., in press.