CATALYTIC TRANSFORMATIONS OF C_3 CYCLIC OLEFINS IN THE PRESENCE OF Ni(0) COMPLEXES.

3. $Ni(PPh_3)_n$ COMPLEXES (n = 3, 4) AS CATALYSTS FOR THE DIMERIZATION AND TRIMERIZATION OF METHYLENECYCLOPROPANE AND REACTION INTERMEDIATES

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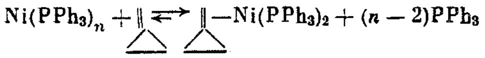
In previous work [1], we described the transformation of methylenecyclopropane (MCP) on $(MCP)Ni(PPh_3)_2$ (Cat-1). Similar reactions of MCP are produced by Ni(0) triphenylphosphine complexes, differing in their ligand environment and method of preparation [2]. The scheme for the catalytic cycle proposed in our previous work [1] involves Cat-1 as the general intermediate. However, the formation of Cat-1 has been established only in two cases: in the reaction of MCP with $Ni(PPh_3)_2$ (η^2-C_2H_4) and in the reduction of the nickel salt of diethylethoxyaluminum in benzene containing MCP and PPh_3 [3].

In the present work, we studied the reaction of MCP with Ni(0) complexes obtained by the reduction of $NiCl_2 \cdot 6H_2O$ by sodium borohydride in the presence of PPh_3 and also with NiL_3 and NiL_4 complexes ($L = PPh_3$). Independent interest is found obtaining new information on the involvement of NiL_2 as an intermediate in the reactions of olefins which proceed by the action of nickel phosphine complexes such as the complex of MCP with NiL_n (n = 3, 4). Thus, we proposed the highly reactive, incompletely coordinated complex, NiL_2, formed during the reactions, participates in the catalytic transformations of MCP along with Cat-1 [1]. The participation of NiL_2 as an intermediate when using phosphine complexes was also proposed in the reactions of aliphatic olefins [4, 5].

According to Holah et al. [6], the reaction of $NiCl_2 \cdot 6H_2O$ with $NaBH_4$ in the presence of PPh_3 in ethanol leads to pyrophoric $[Ni(BH_4)L_3]_2$, which decomposes in organic solvents to give NiL_2 and $L \cdot BH_3$. In order to reduce Ni(II) to Ni(0) and study the possibility of obtaining NiL_2, we modified the procedure and carried out this reaction in benzene–ethanol. In order to remove $L \cdot BH_3$, the precipitate was repeatedly washed with water and ethanol and then recrystallization from ether gave Cat-2.

The ^{31}P–$\{^1H\}$ NMR spectrum of Cat-2 in toluene at –80°C has a multiplet with maxima at δ 24.49, 22.88, and 19.93 ppm with integral intensity ratio 1.2:6.0:1.0. Upon the addition of PPh_3 to the toluene solution of Cat-2, the spectra reveal only a narrow signal at 24.12 ppm, corresponding to NiL_4 [7]. Thus, product Cat-2 is a mixture of Ni(0) triphenylphosphine complexes, including NiL_4, NiL_3 [7, 8], and probably, NiL_2.

The reaction of olefin with NiL_4, NiL_3, and Cat-2 was studied to provide experimental verification of the formation of Cat-1 as an intermediate in the catalytic transformations of MCP in the presence of nickel triphenylphosphine complexes. NiL_3 and NiL_4 were found to react with a five-fold excess of MCP at 20°C in benzene solution, to give complex Cat-1 in 81 and 88% yields, respectively



Cat-1 can be isolated only when the solid starting phosphine complex is treated with a benzene solution of MCP (≥3 moles/liter). The structure of the product, Cat-1, was confirmed by ^1H and ^{31}P–$\{^1H\}$ NMR spectroscopy [3]. Olefinic complex Cat-1 is also formed upon the reaction of Cat-2 with MCP under the conditions described for pure NiL_3 and NiL_4.

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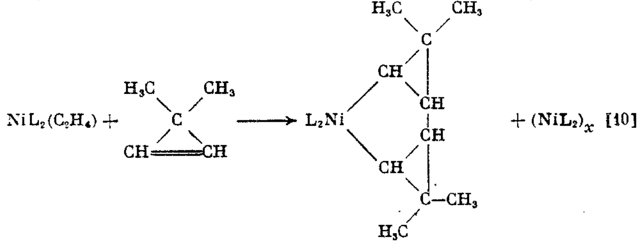
TABLE 1. $^{31}P-\{^1H\}$ NMR Spectra of Ni(0) Triphenylphosphine Complexes Formed in the Substitution Reactions of the Olefin Ligand

Reaction	δ, ppm
$NiCl_2 \cdot 6H_2O + L + NaBH_4 \rightarrow NiL_n$ (n=2–4) benzene–ethanol (present work)	19.9; 22.9; 24.5
$NiL_2(C_2H_4)$ + MCP → NiL_2(MCP) + NiL_n* [3]	20.0–24.1
NiL_2(MCP) → NiL_n* [1] (on Cat-1 at MCP conversions of about 100%)	19.9–24.3
	19.9–24.3

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*Red-brown crystalline Ni(0) complexes.

TABLE 2. Catalytic Properties of Ni(0) Triphenylphosphine Complexes in Benzene at 60°C ($[MCP]_0$ = 1.2 mole/liter, [Ni] = $1.2\text{-}1.4 \cdot 10^{-3}$ mole/liter, 7 h)

Complex	Activity, mole MCP/mole Ni·h	Selectivity, %			Composition, %*				
					dimers		trimers		
		ΣC_8	ΣC_{12}	ΣC_{16+}	(I)	(II)	(III)	(IV)	(V)
$NiL_4+NiL_3+NiL_2$ (Cat-2)	32	30	66	4	28	72	31	63	6
NiL_4	23	29	65	6	29	71	32	60	8
NiL_3	27	32	61	7	29	71	35	56	9
NiL_2 (MCP)	33	32	64	4	27	73	30	60	10

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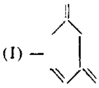
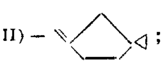
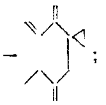
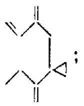
* (I) – ; (II) – ; (III) – ; (IV) – ; (V) – unidentified C_{12} trimers.

Comparison of the spectral parameters of this catalyst and the red-brown crystalline products (Table 1) formed along with the major compounds in the synthesis of complexes containing PPh_3 and MCP or 3,3-dimethylcyclopropene (DMCP) as ligands is in good accord with the conclusion drawn concerning the composition of Cat-2. It has been assumed that the appearance of signals in the $^{31}P-\{^1H\}$ NMR spectra at 20.0-24.2 ppm is related to the formation of Ni(0) phosphine complexes containing NiL_2 in the reaction mixtures [1, 3, 9, 10]. NiL_2 is formed by the decomposition of the metallocycle precursors of the dimers and trimers under these conditions.

The spectral parameters of Cat-2 and Ni(0) triphenylphosphine complexes, which are formed without separation of the metal from $NiL_2 \cdot (\eta^2\text{-}C_2H_4)$ at DMCP conversions close to 100% are similar. $(NiL_2)_x$ is also, in all likelihood, present in this mixture [10].

It is characteristic that the UV and visible spectra for Cat-2 and of the red-brown crystalline products (Table 1) [1] are virtually identical (absorption bands at 372 nm, shoulder at 315 nm, and continuous absorption below 295 nm). As in the case of the complexes described in in our previous work [1], interconversions of Cat-2 and Cat-1 were found. The addition of MCP leads to the instantaneous transition of Cat-2 to Cat-1. The ready formation of Cat-1 is most likely a consequence of the high reactivity of incompletely coordinated NiL_2. The reverse transition of Cat-1 to NiL_2 proceeds more slowly and is observed only at MCP conversions close to 100%.

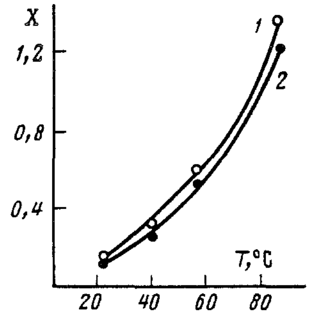


Fig. 1

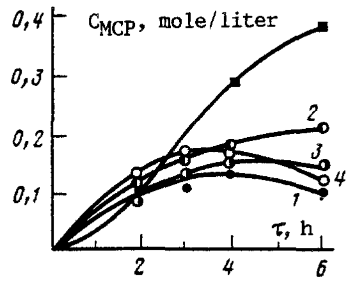


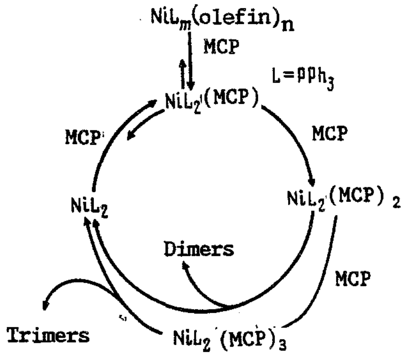
Fig. 2

Fig. 1. Effect of temperature on the mole ratios (X) of the dimers and trimers of MCP in the presence of Cat-2: 1) (I)/(II), 2) ((I) + (II))/((III) + (IV)). Designations as in Table 1.

Fig. 2. Kinetic curves for the consumption of MCP to give the products of its catalytic transformations in the presence of Cat-2: 1) (I), 2) (II), 3) (III), 4) (IV), and 5) oligomers.

A study of the initial catalytic activity and distribution of the MCP transformation products in the presence of Cat-2 and NiL_3, NiL_4, and $NiL_2(MCP)$ complexes (Table 2) indicated the following. Under the conditions studied, NiL_3 is very similar in activity to NiL_4 (27 and 23 moles MCP/mole Ni·h). Cat-1 and Cat-2 display virtually identical activity, which is not markedly greater than that for NiL_3 and NiL_4 (32-33 moles MCP/mole Ni·h). The distribution of the reaction products on all the complexes studied hardly differs. The kinetic curves for the formation and consumption of products of the dimerization and trimerization of MCP on NiL_3, NiL_4, and Cat-2 are analogous to those described for Cat-1 [1] (Figs. 1 and 2). The ratio of dimers and trimers increases with increasing temperature along with an increase in the dimer fraction. The similar changes found in catalyst activity and selectivity in the case of Cat-2 and the pure complexes (Table 2) may be related to the circumstance that both Cat-1 and NiL_2 are intermediates in the MCP reactions. In the case of NiL_3 and NiL_4, a step involving formation of either NiL_2 or Cat-1 must initially occur.

Thus, new evidence was obtained for our previous scheme for the catalytic cycle of MCP transformations by the action of Ni(0) triphenylphosphine complexes [1]. The formation of Cat-1 in the reaction of MCP with NiL_3, NiL_4, and Cat-2 was established and interconversions of Cat-2 and Cat-1 were detected during the reaction. In general form, the scheme may be given as follows:



$m + n = 3, 4$; $n = 0, 1$; $n = 1$, $m = 3, 4$; for $N = 1$, $m = 2$; $NiL_2(MCP)_x$ ($x = 2, 3$) are nickel acyloalkane precursors of the dimers and trimers.

EXPERIMENTAL

The $^{31}P-\{^1H\}$ NMR spectra were taken on a Bruker HX-90 spectrometer in toluene with 85% H_3PO_4 as the external standard at −80°C. The PMR spectra were taken on a Bruker WM-250 spectrometer at 250 MHz in deuterobenzene with benzene as the internal standard and on a WP-200SY spectrometer. The electronic transmission spectra were taken at 190-850 nm on a

Hitachi M-430 spectrometer at 20°C. All the operations on the synthesis, separation of the complexes, and catalytic experiments were carried out in argon using absolute solvents. The gas-liquid chromatographic analysis was carried out as in our previous work [1].

$Ni(PPh_3)_n$ complexes (n = 3, 4; Cat-2) were synthesized by a modification of the method of Holah et al. [6]. A suspension of 31.6 mmoles $NaBH_4$ in 30 ml ethanol was added with stirring over 15 min to 3.8 mmoles $NiCl_2 \cdot 6H_2O$ and 22.9 mmoles PPh_3 in 30 ml 2:1 benzene–ethanol. After 20-30 min, the precipitate was filtered off and dried in vacuum.

The catalyst obtained (5.15 g) was washed with 75 ml water and 125 ml ethanol and dissolved in 250 ml ether. The ethereal solution was evaporated by two thirds and the red-brown precipitate was filtered off, washed with a small amount of ether, and dried in vacuum to give 2.17 g product. The PMR spectrum contains only signals for the phenyl group protons at 6.5-7.9 ppm. The $^{31}P-\{^1H\}$ NMR spectrum contains signals at 24.49, 22.88, and 19.93 ppm. The integral intensity ratio was 1.2:6.0:1.0.

The mixture of complexes obtained (2 g) was dissolved in benzene, evaporated until the onset of crystallization, and treated with ether. The product separated was filtered off, washed with ether, and dried in vacuum to give 0.3 g product. The mother liquor was treated with pentane and the precipitate was dried in vacuum. The $^{31}P-\{^1H\}$ NMR spectrum of the red-brown product contains signals at 24.12, 22.11 and 20.03 ppm and the integral intensity ratio is 3.5:5.0:1.0.

$Ni(PPh_3)_3$ and $Ni(PPh_3)_4$ were synthesized in accord with previous procedures [7, 8].

Reaction of MCP with $Ni(PPh_3)_3$, $Ni(PPh_3)_4$, and Cat-2. A six-fold excess of 3 M MCP solution was added to the nickel complex containing 1.5-3.0 mg-atom nickel and stirred for 1.5 h at 20°C. The yellow crystalline precipitate was filtered off, washed with ether, and dried in vacuum. The yield of (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel was 81-85%. The spectral indices correspond to those described in our previous work [3].

The catalytic transformations of MCP and product identification were carried out as in our previous work [1].

CONCLUSIONS

1. The formation of (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel was established in the reaction of methylenecyclopropane (MCP) with $Ni(PPh_3)_3$, $Ni(PPh_3)_4$, and the catalyst (Cat) obtained by the reduction of $NiCl_2 \cdot 6H_2O$ by sodium borohydride in the presence of PPh_3.

2. $^{31}P-\{^1H\}$ NMR spectroscopy was used to determine that the catalyst was composed of $Ni(PPh_3)_3$, $Ni(PPh_3)_4$, and, probably, $Ni(PPh_3)_2$.

3. Interconversions of the catalyst and (η^2-methylenecyclopropane)bis(triphenylphosphine)nickel were determined during the transformations of MCP, which supports the scheme for the catalytic cycle of MCP reactions by the action of Ni(0) triphenylphosphine complexes.

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