CONCLUSIONS

1. Rhodium and palladium complexes immobilized on amino and aminophosphinated silica gels and polymers containing heterocyclic amine groups catalyze hydrodehalogenation of p-bromotoluene and gem-dihalocyclopropanes by hydrogen transfer from 2-propanol and sodium borohydride.

2. Only partial dehalogenation of gem-dihalogenides occurs with rhodium complexes and 2-propanol. For $NaBH_4$, successive substitution of two halogen atoms occurs. Reduction of gem-dibromides is easier than that of gem-dichlorides. The reaction rate and stereoselectivity depend on the nature and position of the substituent in the cyclopropane.

LITERATURE CITED

1. I. S. Kolomnikov, V. P. Kukolev, and V. Z. Vol'pin, Usp. Khim., 903 (1974).
2. V. F. Dovganyuk, V. I. Isaeva, and V. Z. Sharf, Izv. Akad. Nauk SSSR, Ser. Khim., No. 6, 1223 (1988).
3. V. Z. Sharf, V. F. Dovganyuk, V. I. Isaeva, and B. I. Maksimov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 3, 534 (1989).
4. V. F. Dovganyuk, L. I. Lafer, V. I. Isaeva, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 12, 2660 (1987).
5. G. V. Myasoedova, I. I. Antokolskaya, O. P. Shvoeva, et al., Talanta, 23, 866 (1976).
6. B. N. Laskorin, N. G. Zhukova, O. M. Grishina, et al., Zh. Prikl. Khim., 55, No. 3, 555 (1982).
7. M. Makosza and W. Wawrzyniewic, Tetrahedron Lett., 4659 (1969).
8. O. M. Nefedov, N. N. Novitskaya, and A. D. Petrov, Dokl. Akad. Nauk SSSR, 152, 629 (1963).
9. O. M. Nefedov and R. N. Shafran, Zh. Org. Khim., 37, 1561 (1967).
10. Al-Niami and R. S. Mutana, Z. Naturforsch. 35A, 129 (1980).
11. O. M. Nefedov, M. N. Manakov, and A. A. Ivashenko, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1242 (1962).
12. P. S. Skell and A. Y. Garner, J. Am. Chem. Soc., 78, 5430 (1956).

CATALYTIC ACTIVITY OF NICKEL COMPLEXES IN VINYL HYDROGEN SUBSTITUTION REACTIONS AND STYRENE DIMERIZATION

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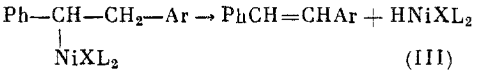
Condensation of arylhalogenides with styrene is an effective method for synthesis of stilbene and its derivatives [1]. The complex $NiCl_2L_2$ (I) (L = tertiary phosphine) in MeCN with a stoichiometric quantity of Zn [2] can be used as a catalyst for this reaction

$$ArX + PhCH = CH_2 \xrightarrow{(I)/Zn} PhCH = CHAr \qquad (1)$$

Zn reduces complex (I) into the active Ni(0) compound (presumably NiL_2), oxidative addition of which to ArX and formation of $ArNiXL_2$ (II) are the first steps in the catalytic process. Decomposition of the addition product of the intermediate (II) to styrene by β-elimination leads to formation of stilbene and the hydride complex (III).



$$\underset{\displaystyle NiXL_2}{Ph{-}\underset{|}{CH}{-}CH_2{-}Ar} \rightarrow PhCH{=}CHAr + \underset{(III)}{HNiXL_2} \qquad (2)$$

The complex (III) catalyzes the dimerization side reaction of styrene [3], as a result of which 1,3-diphenyl-1-butene (DPB) is obtained.

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TABLE 1. Effect of the Ligand L in the $NiCl_2L_2$ Complex (I) on the Yield of Stilbene and DPB*

Expt. No.	L	Yield, mmole	
		stilbene	DPB
1	Bu_3P	0,46	0,03
2	$PhPEt_2$	0,56	0,03
3	Ph_2PEt	0,78	0,11
4	Ph_3P	0,92	0,25
5	$(Ph_2PCH_2)_2$ **	0,53	0,08
6	Cy_3P ***	0,55	0,29

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*0.05 mmole of complex (I) in 3 ml MeCN, mole ratio of reagents (I):PhBr:Zh:$PhCH{=}CH_2$:Py = 1:20:20:80:80, 4 h.
**Corresponds to 2L.
***Cy = cyclohexyl.

TABLE 2. Ni Complexes in the Catalytic Stilbene and DPB Formation Reactions[a]

Expt. No.	Complex,[b] mmole	Styrene, mmole	Yield, mmole	
			stilbene[c]	DPB
1	$ArNiXL_2$[d], 0,05	4	–	–
2	$PhNiClL_2$, 0,2	8	0,084 (0,42)	0,59
3	$PhNiBrL_2$, 0,1	8	0,035 (0,35)	0,18
4	$PhNiClL_2$, 0,05	4	0,81 (16,0)	0,20
5	$PhNiBrL_2$, 0,05	4	0,77 (15,4)	0,17
6	o-$TolNiBrL_2$, 0,05	4	0,77 (15,4)	0,22
7	NiL_4, 0,05	4	0,78 (15,6)	0,18
8	$HNiBrL_2$, 0,05	4	0,45 (9,0)	0,36

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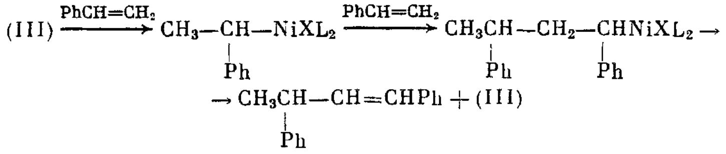
[a] Mole ratio of reagents: Ni:PhBr:Zn:Py = 1:20:20:80, 3 ml MeCN, 4 h, expt. No. 1 was done without Zn, expt. No. 2, 3, without Zn, PbBr, and Py.
[b] L = Ph_3P.
[c] Mole per mole of Ni complex in parentheses.
[d] Ar = Ph, o-Tol; X = Cl, Br.



$$\text{(III)} \xrightarrow{\text{PhCH=CH}_2} \underset{\text{Ph}}{\text{CH}_3\text{—CH}}\text{—NiXL}_2 \xrightarrow{\text{PhCH=CH}_2} \underset{\text{Ph}}{\text{CH}_3\text{CH}}\text{—CH}_2\text{—}\underset{\text{Ph}}{\text{CH}}\text{NiXL}_2 \rightarrow \rightarrow \underset{\text{Ph}}{\text{CH}_3\text{CH}}\text{—CH=CHPh} + \text{(III)} \qquad (3)$$

Reaction (3) is inhibited by pyridine (Py) which also assists reduction by Zn of complex (III) to Ni(0) [2].

We studied the effect of the ligands in complexes (I)-(III) on their activity in the catalysis of the condensation and dimerization reactions which occur in the bromobenzene–styrene–acetonitrile–Py system at 65°C (Table 1).

Py is able to displace phosphine from the coordination sphere of the Ni atom [4]. However, the fact that the nature of the phosphine has an effect on the yield of products indicates that if a similar exchange of ligands occurs it is partial and the catalytic particles are apparently mixed phosphine–Py complexes.

The yield of stilbene (Table 1, expt. No. 1-4) increases as the number of phenyl groups on the phosphine ligand increases which can be a result of increased stability of the catalytic system as a whole due to a lower propensity of the arylphosphines toward oxidation and formation of phosphonium salts, etc. The catalytic activity of complex (I) in this series increases with lowered basicity of the phosphine. This allows the assumption that the oxidative addition step (formation of intermediate (II)), which is favored by donor ligands [5], is not limiting in reaction (1).

TABLE 3. Dimerization of Styrene Using $HNiBr(Cy_3P)_2$*

Expt. no.	Ni complex, mmole	Py, mmole	Zn, mg·at	DBP yield, mmole (mole/mole Ni)
1	0,028	–	–	0,115 (4,1)
2	0,030	–	–	0,135 (4,5)
3	0,037	2	–	0,075 (2,0)
4	0,037	2	0,2	0,079 (2,1)
5	0,018	2	0,45	0,040 (2,2)

*3 ml MeCN, 4 h, 2 mmoles styrene in expt. No. 1, 3-5; 10 mmoles styrene in expt. No. 2.

Stoichiometric reactions (without Zn) of complexes (II) with styrene occur with great difficulty (Table 2). In particular, formation of the corresponding stilbene from $ArNiXL_2$ upon carrying out the reaction in 1.3 M styrene solution is not observed (Table 2, expt. No. 1). In solutions with more concentrated complex (II) and styrene, the yield of stilbene reaches 0.4 mole per mole of Ni complex (expt. No. 2, 3), and DPB is oberved simultaneously. The situation improves markedly in the presence of Zn (expt. No. 4-6) and the yield of stilbene reaches 15-16 moles per mole of Ni complex. Results for various (II) complexes are identical and coincide with those for the NiL_4 complex (expt. No. 7) which should be expected considering the similarity of the corresponding intermediates, explained by the consistent starting ArX substrate (in this case PhBr).

Considering the role of oxidative addition in the mechanism of vinyl substitution which was mentioned above, the data of Table 2 allow the assumption that the limiting step of reaction (1) is the insertion of styrene into the Ar—Ni bond. The $ArNiXL_2$ intermediates which are obtained *in situ* are much more active than (II) complexes which were prepared earlier. Moreover, it is impossible to exclude that the reduction of these by Zn into the Ni(I) complexes (for example, $ArNiL_3$) which are highly active in oxidative addition [6, 7] plays a definite role.

Use of the hydride complex $HNiBr(Cy_3P)_2$ also leads to production of stilbene using Zn (expt. No. 8). This confirms the participation of the latter in the regeneration of the active forms of Ni from the (III) complexes.

The dimerization of styrene also was done without arylhalogenide with the hydride complex (Table 3). In this reaction, the possibility of formation of complex (III) was eliminated and the yield of DBP was lower than in expt. No. 8 (Table 2). The degree of styrene dimerization was changed little with a five-fold increase of its content in the mixture (expt. No. 1, 2). Py lowered the yield of DPB by about half (expt. No. 3) while the presence of Zn practically does not affect the course of reaction (3) (expt. No. 4, 5). Reaction with Py deactivates complex (III) and facilitates its subsequent conversion into the Ni(0) complex.

The effect of the L and X ligands on the styrene dimerization reaction was studied relative to the $HNiXL_2$ complexes which are obtained *in situ* in the ArX-complex (I)—Zn—styrene system (Table 4). The quantity of complex (III) which is formed in this system by reaction (2), is as a rule less than the quantity of starting complex (I) and equivalent to the quantity of stilbene obtained after the same time. Thus, it becomes possible to evaluate the relative catalytic activity of the (III) complexes by the average number of styrene dimerization cycles (n) which is determined from the mole ratio of DPB and the corresponding stilbene, in contrast to previous cases. The yield of the latter, as in the experiments with excess Py (Table 1), is lowered upon substituting phenyl groups on the phosphorus atom in the ligand L by ethyl and cyclohexyl groups. This trend is observed both in the reaction with bromobenzene (PhBr, expt. No. 1, 3, 6, 10) and with p-bromotoluene (p-TolBr, expt. No. 2, 4, 8, 12).

The values of n are sufficiently close for the two indicated arylbromides for a given ligand L. Thus, in both series, similar orders of ligand effects on the catalytic activity of the (III) complexes are observed: (the average value of n for the two series is given in parentheses): $PhPEt_2$ (12) > Cy_3P (8.2) > Ph_2PEt (5.8) ≈ $Ph_2PCH_2CH_2PPh_2$ (5) > Ph_3P (3.3). An increase in the basicity of the phosphines upon replacement of a phenyl group by an ethyl group leads to an increase in n which is probably explained by increased stability (lifetime) of the hydride complex.

TABLE 4. Effect of X and L Ligands on the Activity of the $HNiXL_2$ Complex in the Dimerization of Styrene*

Expt. no.	L	ArX	Yield, mmole		n**
			ArCH=CHPh	DPB	
1	Ph_3P	PhBr	0,06	0,20	3,3
2	»	*p*-TolBr	0,021	0,069	3,3
3	Ph_2PEt	PhBr	0,033	0,14	4,2
4	»	*p*-TolBr	0,019	0,14	7,4
5	$PhPEt_2$	PhCl	0,0005	0,124	240
6	»	PhBr	0,033	0,35	10,6
7	»	»	0,11	0,085	0,8
8	»	*p*-TolBr	0,005	0,068	13,6
9	»	PhI	0,003	0,0055	1,9
10	Cy_3P	PhBr	0,0035	0,027	7,7
11	» ***	»	0,014	0,040	2,9
12	»	*p*-TolBr	0,006	0,052	8,7
13	$(Ph_2PCH_2)_2$	PhBr	0,05	0,30	6
14	»	*p*-TolBr	0,008	0,031	3,9

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*0.05 mmole complex (I) in 3 ml MeCN, 4 h, mole ratio (I):ArX: Zn:$PhCH=CH_2$ = 1:4:4:40.

**Ratio of yields of DPB and corresponding stilbene.

***With a fourfold excess of Py relative to complex (I).

Another trend in the effect of the ligand L on the dimerization of styrene was observed in the reaction which is catalyzed by complex (I) in the presence of excess Py (Table 1): the yield of DPB increased upon replacement of the phosphine alkyl group by phenyl. Undoubtedly, this difference is related to the inhibition of dimerization by Py. The data of Tables 2 and 3 and results of expt. No. 7 and 11 (Table 4) also indicate this. Judging from the trend mentioned above and the data of Table 4, the inhibiting effect of Py weakens as the volume of the ligand L is increased, indicating steric hindrance of the ligand volume. Obviously, this explains the attainment of the highest yield of DBP for the Ni complexes with tricyclohexylphosphine Cy_3P (Table 1, expt. No. 6; Table 2, expt. No. 8).

Comparing the DPB yield data using Cy_3P as ligand L (Table 4, expt. No. 10) with analogous results given in Table 3 (expt. No. 1 and 2), it is easy to see that the dimerization of styrene occurs more effectively in the first case. This confirms the observation stated above about the higher catalytic activity of the Ni intermediates generated *in situ* by comparison with those of the same type synthesized earlier.

The important role of the anionic ligand X was shown based on the $HNiX(PhPEt_2)_2$ complex: the number of dimerization cycles falls in the order $Cl^- \gg Br^- > I^-$ (Table 4, expt. No. 5, 6, 9). This result can be a result of high sensitivity of the dimerization step (insertion of styrene into the H—Ni and C—Ni bonds) to the nature of the X ligand which occupies the position in the complex (III) trans to the H atom. Moreover, it can be proposed that the stability of the (III) complexes toward reduction to the intermediates Ni(I) and Ni(II) decreases markedly in the order $Cl^- > Br^- > I^-$.

EXPERIMENTAL

Py and MeCN were dried by KOH and $CaCl_2$, respectively, and distilled over CaH_2 under Ar. The Ni complexes were obtained by known methods: $(PBu_3)_2NiCl_2$ [8], $(PPhEt_2)_2NiCl_2$ and $(PPh_2Et)_2NiCl_2$ [9], $(PPh_3)_2NiCl_2$ [10], $(dppe)NiCl_2$ [11], $(PCy_3)_2NiCl_2$ [12], $PhNiCl(PPh_3)_2$, $PhNiBr(PPh_3)_2$, o-$TolNiCl(PPh_3)_2$, and o-$TolNiBr(PPh_3)_2$ [13], $HNiBr(PCy_3)_2$ [14], and $Ni(PPh_3)_4$ [15]. All reactions were done in an argon atmosphere.

A mixture of arylhalogenide, styrene, Zn dust, Py (if present, and Ni complex in 3 ml MeCN was stirred for 4 h at 65°C. Naphthalene was added to the reaction mixture as an internal standard and the mixture was analyzed by GLC (Tsvet-110 chromatograph, 3 × 2000 mm column, 3% SE-30 on chromaton N-super, He carrier gas). The quantities of stilbene and DPB formed are given in the Tables.

CONCLUSIONS

1. The complexes $ArNiXL_2$ and $HNiXL_2$ (X is halide, L is tertiary phosphine) in the presence of zinc catalyze the condensation of bromobenzene with styrene (stilbene formation).

2. The yield of stilbene and 1,3-diphenylbutene, the dimerization product of styrene, in the presence of pyridine is lowered according to the substitution of phenyl groups on the phosphorus ligand L by alkyl (ethyl, cyclohexyl) groups.

3. Change of triphenylphosphine to phenylethylphosphines and tricyclohexylphosphine in the hydride complex $HNi(X)(PR_3)_2$, the catalytic activity of which falls in the order $X = Cl^- \gg Br^- > I^-$, favors the dimerization of styrene in the absence of pyridine.

LITERATURE CITED

1. R. F. Heck, Org. React., 27, 345 (1982).
2. S. A. Lebedev, V. S. Lopatina, R. S. Sorokina, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2508 (1987).
3. L. I. Red'kina, K. L. Makovetskii, E. I. Tinyakova, and B. A. Dolgoplosk, Dokl. Akad. Nauk SSSR, 186, No. 2, 397 (1969).
4. Y. Nakamura, K. Maruya, and T. Mizoroki, Bull. Chem. Soc. Jpn., 53, No. 11, 3089 (1980).
5. G. Henrici-Olive and S. Olive, Monograph in Modern Chemistry, Vol. 9: Coordination and Catalysis, Verlag Chemie, Weinheim (1977).
6. I. Colon and D. R. Kelsey, J. Org. Chem., 51, No. 14, 2627 (1986).
7. C. Gosdeu, K. P. Healy, and D. Pletcher, J. Chem. Soc., Dalton Trans., 972 (1978).
8. K. A. Jensen, Z. Anorg. Allg. Chem., 229, 265 (1936).
9. R. G. Hayter and F. S. Humiel, Inorg. Chem., 4, 12, 1701 (1965).
10. L. M. Venanzi, J. Chem. Soc., 719 (1958).
11. G. R. Van Hecke and W. D. Horrocks, Inorg. Chem., 5, No. 11, 1968 (1966).
12. K. Issleib and A. Brack, Z. Anorg. Allg. Chem., 277, 258 (1954).
13. M. Hidai, T. Kashiwagi, T. Ikenchi, and Y. Uchida, J. Organomet. Chem., 30, 279 (1971).
14. A. N. Nesmeyanov, L. S. Isaeva, and L. N. Morozova, Inorg. Chim. Acta, 33, L173 (1979).
15. R. A. Schunn, Inorg. Synth., 13, 124 (1972).

METHYLATION OF PHENOL BY METHYL FORMATE

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547.562.1

The development of the industrial manufacture of formic acid from CO and H_2O has also made methyl formate (MF), an intermediate in this high-tonnage synthesis, available [1]. Unlike that of many other esters, the reactivity of MF has been studied insufficiently. For this reason, we investigated the reaction of MF with phenol in the presence of acid catalysts. We can assume that in this case reactions are possible with the participation of hydrogen both in the hydroxyl group and of the aromatic ring.

EXPERIMENTAL

The MF was boiled over anhydrous $MgSO_4$ and distilled with a fractionating column. Freshly distilled phenol was used. Fused $ZnCl_2$, $C_4F_9SO_3H$, $p\text{-}CH_3{-}C_6H_4SO_3H \cdot H_2O$, tungstosilicic acid $H_8[Si(W_2O_7)_6] \cdot xH_2O$, tungstophosphoric acid $H_7[P(W_2O_7)_6] \cdot xH_2O$, KU-23, and zirconium oxide were used as catalysts [2]. The zirconium oxide was prepared by dissolving ZrO_2 with boiling in concentrated H_2SO_4 and hydrolyzing the obained zirconium sulfate with an aqueous ammonia solution. The zirconium hydroxide was filtered, washed with water, and dried for 10-15 h at 373 K. The ground hydroxide was treated with a 0.5 M H_2SO_4 solution (30 ml of a 0.5 M H_2SO_4 solution per 2 g of $Zr(OH)_4$) and calcined in a muffle furnace at 773-923 K.

The experiments were carried out in an autoclave made of stainless steel with an electrically heated 50 cm^3 vessel equipped with a reflux condenser, manometer, and sampling valve. The temperature in the reaction zone was monitored with a thermocouple connected to a KSP-005 potentiometer. The reaction products were analyzed with a Tsvet-100 chromatograph with a thermal-conductivity detector and a 2 m × 3 mm column filled with Polysorb-1. The feed

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