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TRIPHENYLPHOSPHINE COMPLEXES OF RHODIUM AND IRIDIUM AS NEW HOMOGENEOUS CATALYSTS FOR THE SYNTHESIS OF METHYL N-PHENYLCARBAMATE BY CARBONYLATION OF NITROBENZENE IN METHANOL

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Urethanes are formed by the catalytic carbonylation of nitrobenzene in alcohols:

$$C_6H_5NO_2 + 3CO + ROH \rightarrow C_6H_5NHCOOR + 2CO_2$$

The known homogeneous catalysts of this reaction are

$$RhCl_3,\ [Rh\,(CO)_2\,Cl]_2,\ Rh_6(CO)_{16},\ [C_8H_{12}RhCl]_2$$

in whose presence at 150-170° and a CO pressure of 80-150 at (technical atmosphere) were synthesized the methyl, ethyl, butyl, and phenyl N-phenylcarbamates in 10-82% yields [1, 2].

We established that the triphenylphosphine complexes of Rh and Ir are active homogeneous catalysts of this reaction (Table 1). Nitrobenzene at 180° and a CO pressure of 60 at undergoes 15-37% conversion to give an 8-29% yield of methyl N-phenylcarbamate when based on the starting nitrobenzene. The efficiency of the complexes as catalysts changes in the order:

$$RhH\,(CO)\,(PPh_3)_2 \approx RhCl\,(CO)\,(PPh_3)_3 > IrH\,(CO)\,(PPh_3)_3 > IrH_2(CO)(PPh_3)_3 \approx IrCl\,(CO)\,(PPh_3)_2.$$

In contrast to Rh, in the presence of the Ir catalysts a substantial amount of aniline is formed along with the carbamate. A possible route for obtaining aniline in carbonylation reactions was discussed by us in [3].

The yield of the carbamate drops to 1% when the CO pressure is decreased from 60 to 15 at.

EXPERIMENTAL

The Rh and Ir complexes were synthesized as described in [4-6].

The experiments were run in a rotated steel autoclave fitted with a glass insert, into which were charged 2 ml of a 4.8% solution of $PhNO_2$ in MeOH, 0.1 g of $FeCl_3$, and either the Rh or Ir complex. Then the autoclave was purged with CO and heated for 20 min at 180° under a CO pressure of 15-60 atm. The reaction products were analyzed by GLC as described in [7].

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TABLE 1. Carbonylation of Nitrobenzene in Presence of Rh and Ir Complexes (180°C, pressure 60 at, reaction time 20 min)

Complex	Amount of catalyst, mg	Nitrobenzene conversion, %	Yield, in % of starting $PhNO_2$		Catalyst efficiency, g of carbamate/g of Rh(Ir)·min
			carbamate	aniline	
$IrCl(CO)(PPh_3)_2$	23	15	8	4	16,7
$IrH_2Cl(PPh_3)_3$	30	24	8	3	16,7
$IrH(CO)(PPh_3)_3$	30	22	10	5	20,0
$RhH(CO)(PPh_3)_3$	27	34	28	0	57,0
$RhCl(CO)(PPh_3)_2$	28	37	29	0	58,0

CONCLUSIONS

The Ph_3P complexes of Rh and Ir are active homogeneous catalysts for the synthesis of methyl N-phenylcarbamate by the carbonylation of $PhNO_2$ in MeOH.

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REACTION OF PHENYL GLYCIDYL ETHER WITH TRIPHENYL ISOCYANURATE

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A study of the behavior of the triglycidyl esters of isocyanuric acid (TGEIA) when heated by the IR spectroscopy method disclosed that besides polymerization, the oxirane ring reacts with the isocyanurate ring (ICR). On the basis of the previously observed facts [1-4] that epoxide groups during their opening can be "inserted" into molecular chains across such hetero bonds as CO–O, CO–NR, Si–OAr, Si–NRAr, and also the fact that the ICR contains the NR–CO–NR fragment, analogous to one of these bonds, it may be assumed that the reaction of the ICR with the epoxide group can also go via the route of the insertion reaction to give the urethane fragment. The IR spectral data for the products of heating the TGEIA, which disclose a decrease in the band of the ICR and the appearance and growth of new bands, in particular a band at 1745 cm^{-1}, which is characteristic for urethane compounds, do not contradict this assumption.

To ascertain the reaction course and the structure of the formed compounds, we studied the model reaction of triphenyl isocyanurate (TPI) with phenyl glycidyl ether (PGE), taken in a 1:3 mole ratio on the assumption that the three reactive sites in the ICR have the same reactivity toward the PGE. The reaction was run at 230°C for 10 h. A comparison of the IR spectra of the starting mixture and after heating indicates a nearly com-

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