

# HETEROGENIZED TRANSITION METAL COMPLEXES AS CATALYSTS FOR SYNTHESIZING METHYLPYRIDINES FROM ACETALDEHYDE AND AMMONIA

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*The synthesis of methylpyridines from acetaldehyde and ammonia in the presence of N- and F-containing heterogenized transition metal complexes is studied by a pulse microcatalytic method. A correlation between the donor-acceptor properties of the ligand, of the complexed metal, and of the catalytically active complex is found using  $^{31}\text{P}$  NMR. The reaction direction depends on the properties of the solvent used to heterogenize the complex on the carrier.*

Transition metal complexes over the last decade have become of interest in organic synthesis [1], in particular, the synthesis of methylpyridines. This is due to the fact that known methods for preparing them are unacceptable from an industrial viewpoint or are not selective enough. Such syntheses are based on intramolecular cyclization and heterocyclization involving two or more molecules activated via complexation to transition metals. Complexes of Co [2], Ni [3], and Pd [4] are usually used as the catalysts. We have previously demonstrated that the synthesis of methylpyridines from acetaldehyde and ammonia is catalyzed by Pd complexes containing S [5]. The products contain up to 85 mass % methylpyridines. Therefore, the catalytic activity of heterogenized complexes of several transition metals with N- and F-containing ligands should be studied.

The present article reports on the synthesis of methylpyridines from acetaldehyde and ammonia in the presence of N- and F-containing complexes of general formula  $\text{PdL}_2\text{Cl}_2$ , where L = 2-amino-2-hydroxymethyl-1,3-propanediol (I), 3-aminocoumarin (II),  $\text{Ph}_3\text{P}$  (III),  $\text{Bu}_3\text{P}$  (IV), and  $\text{Ph}_3\text{PO}$  (V), that are deposited on  $\text{Al}_2\text{O}_3$  with the tridentate ligand 4-(2-pyridylazo)resorcinol (PAR) (VI),  $\text{Pd}(\text{PAR})\text{Cl}$ .

The effect of the properties of the complexed metal on the yield of methylpyridines was studied using  $\text{Ph}_3\text{P}$  complexes of Co, Ni, Cu, and Pt.

The methylpyridines were synthesized at 40-180°C with arbitrary contact times 0.25-2.0 sec and at acetaldehyde:ammonia (1-4):(4-1). The concentration of air in the starting material was ~20% and was held constant.

The principal products, like for Pd complexes containing S, are pyridine, methylpyridines with predominantly 4-methylpyridine (up to 83 mass %), acetonitrile (less than 6 mass %), aldimine (4-7 mass %), and a number of unidentified oxidation and amination products in small concentrations (0.1-2.0 mass %). The activities of the catalysts were compared using the average of their first 5-7 pulses. The degree of conversion of the starting aldehyde depends little on the properties of the complex and varies in the range 98-100%. The ammonia is completely converted.

The results are plotted in Figs. 1 and 2. It can be seen that the temperature dependence of 4-methylpyridine formation for all studied catalysts with N-containing Pd complexes (curves 1, 2, 6) has a maximum, the position of which is determined by the properties of the complex. Whereas the maximum for the catalyst containing VI is observed at 60°C, use of complexes of II and I produces maxima at 100°C and 120°C, respectively. Increasing the temperature to 160-180°C reduces 4-methylpyridine formation to 51-53 mass % owing to oxidation and amination. The studied catalysts fall in the order I > II > VI for 4-methylpyridine formation. The concentrations of 2- and 3-methylpyridine and pyridine are small, less than 2-5%. An examination of the literature [6] on the donor properties of the functional groups through which the metal is coordinated revealed that the level of catalytic activity increases as the donor ability increases on going from pyridine in VI to the amino group in I. The decrease in the energy of the metal-ligand bonds and the selective labilization leading to ligand exchange explain such a correlation.

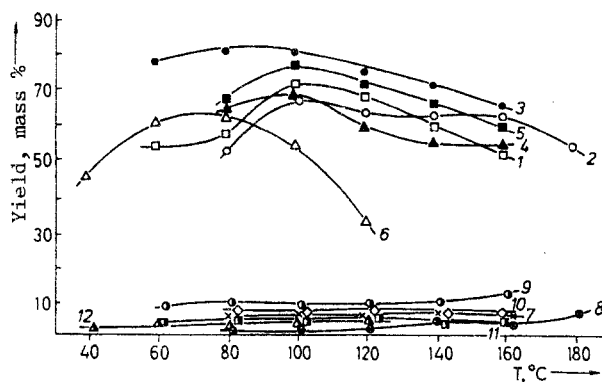


Fig. 1. Dependence of 4-methylpyridine (curves 1-6) and acetonitrile (curves 7-12) formation on temperature: I (1,7), II (2, 8), III (3, 9), IV (4, 10), V (5, 11), VI (6, 12).

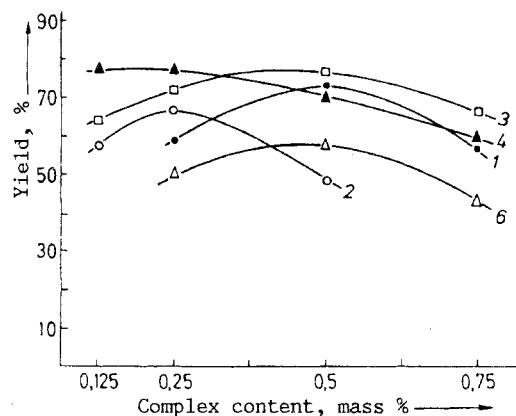


Fig. 2. Dependence of 4-methylpyridine formation on content of complex in the catalyst.

The content of aldimine, an intermediate in the synthesis of methylpyridines, increases in the range 40-180°C from 2 to 13 mass % regardless of the complex used. This agrees with results obtained on catalysts with S-containing complexes [5]. The parallel reaction leading to acetonitrile formation is of little importance (Fig. 1, curves 7-12). The acetonitrile concentration is less than 5% and changes little as the temperature increases.

The optimal Pd content in the catalytic systems is 0.25-0.5 mass % of the support mass (Fig. 2). Both decreasing and increasing the amount of complex on the support decreases the catalyst activity for the desired 4-methylpyridine. In the first instance, the surface coverage of the oxide by the complexes is probably not optimal and a part of the support catalyzes the oxidation and amination. Depositing more than the optimal amount of complex probably leads to the formation of multiple layers. The active centers responsible for methylpyridine formation are blocked by the excess of the complex.

The greatest degree of 4-methylpyridine production occurs for all complex catalysts at contact times of 1 sec. Reducing the contact time by half causes aldimine (up to 10 mass %) to accumulate on the catalysts whereas increasing the contact time to 1.5 sec enhances amination and oxidation. Distinct dependences on the contact time and amount of deposited complex were not observed for acetonitrile formation.

It seemed interesting to compare the catalytic activity of N- and F-containing Pd complexes in which the ligand heteroatoms have different electronegativities and donor-acceptor properties. The experimental conditions were analogous. The results are plotted in Fig. 1 (curves 3-5) and indicate that the temperature dependence of methylpyridine synthesis has a maximum near 100°C, like for the use of N-containing complexes. Further increasing the temperature to 160°C causes the content of 4-methylpyridine on the catalysts to fall owing to more extensive oxidation and amination. Changing from the butyl

substituent in  $\text{Pd}(\text{Bu}_3\text{P})_2\text{Cl}_2$  to phenyl in  $\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$  increases the catalytic activity. The catalytic activity of the F-containing complexes falls in the order III > V > IV (order 2).

The activity of the F-containing complex catalysts differs owing to the different degree to which electron density is transferred from the heteroligand to the metal. This is confirmed by  $^{31}\text{P}$  NMR spectroscopy of the ligands and the corresponding complexes (table data) since the chemical shifts can be considered a measure of the change of electron density in the ligand caused by the structural reorganization after complexation. For  $\text{Pd}(\text{Bu}_3\text{P})_2\text{Cl}_2$ , the signals of the P atom shift to weak field by 11.7 ppm after coordination. This is probably due to shielding by the butyl ligand owing to a positive inductive effect. For  $\text{Pd}(\text{Ph}_3\text{PO})_2\text{Cl}_2$  and  $\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$ , the shift to weak field is 2.5-3.0 times greater, 26.0 and 31.4 ppm, respectively. This is consistent with little influence of the phenyl groups on the Pd-P coordination. The extensive transfer of electron density from P to Pd in the last two complexes is consistent with the higher catalytic activity of their systems. A comparison of the yield of 4-methylpyridine on the N- and F-containing complexes, which have heteroatoms with different donor-acceptor properties, revealed the overall order of catalyst activity ( $100^\circ\text{C}$ ) to be III > V > I > IV > II > VI (order 3). The resulting activity order suggests that the Pd complexes with phosphine ligands are catalytically more active compared with the complexes of the amino derivatives. However, the phosphines are less basic than the amines owing to the diffuseness of the P bonding orbitals and the lower electronegativity compared with N.

The catalytic activity determined by the rate of ligand exchange depends on the trans-effect of the ligand. It has been demonstrated [7] based on an analysis of much experimental data for mixed-ligand complexes of Pt that phosphines have the greatest trans-effect whereas aliphatic amines and pyridine and its derivatives are intermediate. The presence of low-lying vacant *d*-orbitals on P that are absent on N give the Pd-P bonds more double-bond character compared with the Pd-N bonds. As a result, the labilizing effect of the P ligand is greater and the catalytic activity of the corresponding complex is greater.

It seemed interesting to study the effect of the transition metal on the extent and direction of the methylpyridine synthesis. Therefore, catalysts containing the  $\text{Ph}_3\text{P}$  complexes of Co, Ni, Cu, and Pt of general formula  $\text{Me}(\text{Ph}_3\text{P})_2\text{Cl}_2$  deposited on  $\text{Al}_2\text{O}_3$  from DMF to give 0.25 mass % were prepared. These complexes, including the Pd one, are unsaturated 16-electron square-planar complexes [8]. The exception is the Co complex, the outer shell of which has only 15 electrons.

The  $\text{Ph}_3\text{P}$  ligand was chosen since P-containing structures can stabilize complexes in a certain metal oxidation state. The experimental conditions (0.25 mass % deposited complex, 1 sec contact time, acetaldehyde:ammonia:air = 1:4:1) were determined using results for the F-containing complexes of Pd. The principal product regardless of the complexed metal is 4-methylpyridine, the temperature dependence of the yield of which is plotted in Fig. 3. The temperature dependences vary little on going from one complex to another. The maximum amount of 4-methylpyridine on the catalysts for the Pd, Pt, and Cu complexes occurs at  $80^\circ\text{C}$ ; for Co and Ni,  $100^\circ\text{C}$ . The yield of 4-methylpyridine is very similar for the studied complexes. The scatter of the values is in the range 10-12%. An analysis of the  $^{31}\text{P}$  NMR of the complexes (table data) indicates that the complexes have different chemical shifts even if the ligand environment is the same and the same amount of electron density is transferred from P to the metal. The increased shielding in the Co, Ni, and Cu complexes (strong-field shift) is probably due to backbonding from the metal to the vacant P orbital. Weak-field chemical shifts are observed for the Pd and Pt complexes. The value for Pd is almost twice as large as for Pt. The literature suggests [9] that this is probably due to the fact that the resulting donor properties of the metals decreases on going to the right of the periodic table. Metals of Group 10 (Pd) are slightly poorer donors than the higher- and lower-lying neighbors (Pt). A comparison of the donor properties of the examined metals and the catalytic activity of their complexes for synthesizing methylpyridines showed that the latter depends little on the donor properties of the complexed metal.

The catalytic properties of the complex are probably elicited primarily by a mutual influence of the ligands that is based on their donor-acceptor properties. Two mechanisms are examined. The first involves transfer through the central atom (directed trans-effect); the second, a direct ligand-ligand interaction not previously appreciated (undirected effect) [7]. Such an interaction can arise if empty and rather diffuse orbitals are present on one of the interacting ligands and the other has orbitals with electron pairs. Groups with a strong trans-effect ( $\text{Ph}_3\text{P}$ ) that are coordinated through the P atom can form undirected donor-acceptor bonds with *cis*-ligands. Ligands containing S, P, and other elements with vacant *d*-orbitals are very effective as acceptors. Indeed, the 3*d*-orbitals of P are spatially oriented such that they can form bonds to both neighboring ligands in square-planar complexes and the entering group in the intermediate. It is possible that complexes containing ligands with a strong trans-effect can have both a directed and undirected effect. However, the latter is a requisite effect for catalysis.

This is indirectly confirmed by results for the catalytic activity of the Ni  $\text{Ph}_3\text{PO}$  complex on 0.25 mass %  $\text{Pd}(\text{Ph}_3\text{PO})_2\text{Cl}_2-\text{Al}_2\text{O}_3$ . The yield of 4-methylpyridine with this catalyst is less than on the  $\text{Ph}_3\text{P}$  Ni complex (Fig. 3, curve b), 35-55 mass %. Using the P orbitals to interact with the O atom in  $\text{Ph}_3\text{PO}$  decreases its effect on the other ligands in the

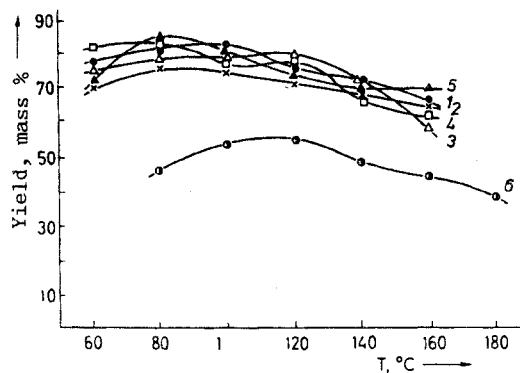


Fig. 3. Temperature dependence of 4-methylpyridine formation in  $\text{Ph}_3\text{P}$  complexes of transition metals and the  $\text{Ph}_3\text{PO}$  complex of Ni:  $\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$  (1),  $\text{Pt}(\text{Ph}_3\text{P})_2\text{Cl}_2$  (2),  $\text{Co}(\text{Ph}_3\text{P})_2\text{Cl}_2$  (3),  $\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2$  (4),  $\text{Ni}(\text{Ph}_3\text{PO})_2\text{Cl}_2$  (5).

complex. This decreases their lability and decreases the catalytic activity. Furthermore, it should be emphasized that the chemical shifts in the NMR spectra of organometallic complexes are determined not only by the donor–acceptor properties of the separate components but also by the order of other parameters. Therefore, any correlations based on them require additional confirmation.

The effect of the solvent from which the complex was fixed to  $\text{Al}_2\text{O}_3$  on the direction and extent of the methylpyridine synthesis was studied. The experiments were carried out in the presence of the Pd  $\text{Ph}_3\text{P}$  complex under the conditions given above. The solvents were DMF and DMSO. The temperature dependences of the total pyridine content are plotted in Fig. 4. It follows that the properties of the solvent have a significant effect on the direction of the oxidative condensation of acetaldehyde and ammonia. As previously demonstrated, the principal product after deposition of the Pd complex on  $\text{Al}_2\text{O}_3$  from DMF is 4-methylpyridine in up to 82 mass % yield. The concentrations of other methylpyridines are less than 3–7 mass %; acetonitrile, ~3 mass %. On going from DMF to DMSO, the heterocyclization produces higher pyridine homologs such as lutidines and collidines with the latter dominating. The total yield of substituted pyridines at 100°C is 83 mass % for 100% conversion of the starting material; of acetonitrile, 4.5 mass %. The catalytic activity of the complex deposited from DMF at 80°C is noticeably greater (89% vs. 66% for DMSO). However, increasing the temperature further to 160°C evens out their activity for the pyridine derivatives.

As previously demonstrated [10], ligand is replaced by solvent during heterogenization of the complex in solution. Since the donor numbers of DMSO (29.8) and DMF (26.6) [11] and their positions in the trans series are similar, the total activities of the catalysts obtained from them are also similar. Moreover, adding a S compound instead of an amide to the Pd complex probably causes the energy levels in the complex to change. The process does not stop with formation of the intermediate trimer, which produces the methylpyridines, but proceeds further to give lutidines and collidines.

## EXPERIMENTAL

The N-containing Pd complexes [12–15] and the P-containing transition metal complexes [15–17] were synthesized using published methods. The composition and structure of the complexes were established by elemental and thermographic analyses and IR spectroscopy.

The catalysts containing Pd complexes were prepared by constructing the complex on the surface of hydroxylated  $\text{Al}_2\text{O}_3$ . The starting compound was  $\text{K}_2\text{PdCl}_4$  and the calculated amount of ligand in the appropriate solvent. The catalysts based on the Co, Ni, Cu, and Pt complexes were deposited on  $\text{Al}_2\text{O}_3$  by impregnation. Samples were dried at 160°C for DMF and at 90°C for DMSO.

The pulse microcatalytic apparatus, the chromatographic methods, and the starting material composition have previously been described [5].

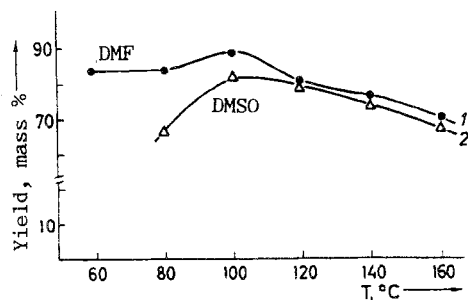


Fig. 4. Temperature dependence of pyridine-derivative formation on  $\text{Pd}(\text{Ph}_3\text{P})_2\text{Cl}_2$  as a function of solvent.

The  $^{31}\text{P}$  NMR spectra of the complexes and P-containing ligands were recorded on a SXR-200 Bruker instrument at 81.3 MHz with  $\text{H}_3\text{PO}_4$  standard.

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