BIPHASE REDUCTION OF HEPTANAL AND CYCLOHEXANONE BY SODIUM FORMATE CATALYZED BY ETHER-PHOSPHINE RUTHENIUM(II) COMPLEXES

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$RuCl_2[P(C_6H_5)_2OCH_2CH_2OCH_3]_2$ has efficiently catalyzed the reduction of cyclohexanone and heptanal by sodium formate in chlorobenzene–water, using cetylpyridinium bromide as the phase transfer catalyst. In both cases, the reduction was first order both in the substrate and in the initial concentration of the catalyst. The catalyst activity in the aldehyde reduction could be increased by the addition of the free ligand while in the ketone reduction the ligand in excess decreased the reaction rate. Several other phosphines of the type $P(C_6H_5)_2L$ where L = C_6H_5, C_4H_9, $C_2H_5OCH_2CH_2$, $C_4H_9OCH_2CH_2$, 1,4-dioxanemethyl, tetrahydrofurfuryl, and $P(i\text{-}C_3H_7)_3$) gave the less efficient catalysts. Kinetic and activation data for the reduction of both substrates are reported.

In recent years, an increased attention in the chemistry of transition metal-phosphine complexes has been paid to the ligands containing in addition to the soft phosphorus also the hard oxygen or nitrogen atom. These were expected to behave as polydentates, the relatively stable metal–phosphorus coordination being accompanied by a weak metal–hard base bonding. In the case of ether-phosphines (further denoted as P,O ligands) their bifunctionality has been observed in complexes of several transition metals, including tungsten[1,2], platinum[3,4], palladium[3,5,6], iridium[7], rhodium[3,8,9], and ruthenium[3,10].

However, depending on the oxidation state of transition metal and the structure of the complex, the metal–oxygen bond could undergo cleavage, leaving the phosphine as the monodentate ligand. The example of such a behaviour has recently been reported for several platinum complexes[4].

It is widely accepted that the hemilability of these ligands could have favourable effect in transition metal-catalyzed processes where an even weak additional coordination can stabilize vacant site(s) formed during catalytic cycle. However, when compared to the studies devoted to the chemistry of transition metal complexes containing ether-phosphines (and other ambivalent ligands – for a recent review see ref.[11]), much less attention has been focused on their application as the catalysts. A systematic investigation has seldom been made, except for methanol carbonylation (cf. ref.[8] and references given therein). Briefly mentioned were the two-phase reduction of bromobenzene with sodium hydride[12] and of allyl acetate[13], allyl chloride[13], and chloronaphthalene[5] with sodium formate, hydrogenation of hexyne to hexenes[6], all catalyzed by Pd complexes, water gas shift reaction[2], hydrogenation of hexene to hexane[14], and hydrocarbonylation of methyl acetate[8], all catalyzed by Rh complexes, hydrogenation of phenylacetylene in the presence of Ir catalysts[15], and finally hydrogenation of acetaldehyde with Ru-P,O complexes[16] as the catalysts.

Within the framework of an intended study of poly(oxyalkylene)phosphines as potential ligands of water soluble catalysts[17], we have examined more extensively also the behaviour of the parent phosphines of the type $P(C_6H_5)_2OCH_2CH_2OR$ (R = alkyl). In the present work we report on the two phase hydrogen transfer reduction of the C=O group by sodium formate[18,19] catalyzed by several ruthenium(II) ether-phosphine complexes.

EXPERIMENTAL

Chemicals

Heptanal (purum; Fluka), 1-heptanol (purum; Reakhim, Russia), cyclohexanone, cyclohexanol, and sodium formate (all analytical grade; Lachema Brno) were commercial products as indicated. Heptanal and cyclohexanone were redistilled under nitrogen, and the GLC pure medium fraction of both was used in the experiments. PEG 300 and PEG 1000 (purum; NCHZ Novaky, The Slovak Republic), methyltrioctylammonium chloride (purum; Fluka), and cetylpyridinium bromide (purum; Lachema Brno) were used as obtained.

Phosphines

Triphenylphosphine, l,2-bis(diphenylphosphino)ethane (both purum; Fluka), butyldiphenylphosphine (96%; Aldrich), and triisopropylphosphine (for synthesis; Merck) were used without further purification.

2-Methoxyethyl(diphenyl)phosphine was obtained by the reaction of lithium diphenylphosphide with 2-chloroethyl methyl ether, using the reported procedure[20] (yield 26%, b.p. 150 – 156 °C/8 Pa; for $C_{15}H_{17}OP$ (244.3) calculated: 73.75% C, 7.02% H, 12.68% P; found: 73.50% C, 6.91% H, 12.83% P). The same procedure using the corresponding chloroethyl ethers[21], was utilized to prepare 2-ethoxyethyl(diphenyl)phosphine (yield 47%, b.p. 133 – 140 °C/5 Pa; for $C_{16}H_{19}OP$ (258.3) calculated: 74.39% C, 7.41% H, 11.99% P; found: 74.52% C, 7.49% H, 11.74% P), and 2-butoxyethyl(diphenyl)phosphine (yield 53%, b.p. 145 – 152 °C/2 Pa; for $C_{18}H_{23}OP$ (286.3) calculated: 75.49% C, 8.10% H, 10.82% P; found: 75.40% C, 8.16% H, 10.80% P).

Diphenyl(tetrahydrofurfuryl)phosphine[22] and 1,4-dioxanemethyl(diphenyl)phosphine[23] were obtained by the reaction of lithium diphenylphosphide (prepared by lithiation of triphenylphosphine) with 2-chloromethyltetrahydrofurane (purum; Merck) and 2-chloromethyl-1,4-dioxane[24], respectively. Physico-chemical data of the products obtained agreed well with those reported.

Ruthenium-Phosphine Complexes

trans-Dichloro-*cis*-bis[(2-methoxyethyl)diphenylphosphine-*O,P*]ruthenium(II) (*I*) was prepared[16] by the reaction of $RuCl_3 . 3 H_2O$ (purum; Fluka) with 2-methoxyethyl(diphenyl)phosphine (76% yield of the red needle-like crystals melting at 145 °C with decomposition (reported[16] 147 °C). Mass spectrum: 660 (M^+, ^{35}Cl). For $C_{3O}H_{34}Cl_2O_2P_2Ru$ (660.4) calculated: 10.73% Cl, 9.38% P, l5.30% Ru; found: 11.23% Cl, 9.72% P, 14.97% Ru. ^{13}C NMR spectra of the complex dissolved in C_6D_6 agreed with the proposed structure.

trans-Dichloro-*cis*-bis[diphenyl(tetrahydro-2-furanylmethyl)diphenylphosphine-*O,P*]ruthenium(II) (*II*) was obtained[16] in 70% yield by an analogous reaction from ruthenium trichloride and diphenyl-(2-tetrahydrofurfuryl)phosphine (dec. temp. 201 °C (reported[16] 205 °C and 198 °C). Mass spectrum: 712 (M^+, ^{35}Cl). For $C_{34}H_{38}Cl_2O_2P_2Ru$ (712.6) calculated: 9.95% Cl, 8.69% P, l4.18% Ru; found: 10.19% Cl, 9.13% P, 14.35% Ru.

trans-Dichloro-*cis*-bis[(1,4-dioxanemethyl)diphenylphosphine-*O,P*]ruthenium(II) (*III*) was obtained in 80% yield by the exchange of the ligand in $RuCl_2[P(C_6H_5)_3]_2$ for 1,4-dioxanemethyl(diphenyl)phosphine, as reported[16] (dec. temp. 199 °C (reported[16] 197 °C). Mass spectrum: 744 (M^+, ^{35}Cl). For $C_{34}H_{38}Cl_2O_4P_2Ru$ (744.6) calculated: 9.52% Cl, 8.32% P, 13.57% Ru; found: 9.67% Cl, 8.72% P, 13.16% Ru.

Tris(triphenylphosphine)ruthenium(II) chloride (*IV*) was a commercial product (Aldrich).

$RuCl_2[P(C_6H_5)_2CH_2CH_2OCH_3]_2$

I

$RuCl_2[P(C_6H_5)_2CH_2C_4H_7O]_2$

II

$RuCl_2[P(C_6H_5)_2CH_2C_4H_7O_2\text{-}1,4]_2$

III

$RuCl_2[P(C_6H_5)_3]_3$

IV

Reduction with Ruthenium Catalysts Prepared in situ

A. Ruthenium(III) chloride trihydrate (10.4 mg, 0.045 mmol), phosphine (0.8 – 0.9 mmol), water (5 ml, degassed in vacuo with ultrasound mixing), organic solvent (0.2 ml), phase transfer catalyst (0.2 – 0.5 mmol) and 2 M HCOONa solution (2.5 ml) were placed into the reactor and rapidly warmed up with stirring to the reaction temperature (in 3 min) at which the reaction was started by the addition of the substrate (1.9 mmol).

B. The organic solvent (2.5 ml), water (5 ml), 2 M HCOONa solution (2.5 ml), phase transfer catalyst (0.18 mmol), ruthenium-phosphine complex *IV* (10.4 mg, 0.045 mmol), and a given phosphine in excess (P/Ru molar ratio 8 – 12 : 1) were stirred under reaction conditions for a given time, followed by the substrate addition which started the reduction.

Two Phase Reduction – General Procedure

The reduction was performed in a 25 ml-glass tubular flat-bottom reactor, the side walls of which were wedge-cut along their axis. The reactor was provided with a silicone-covered septum-inlet adapter and a magnetic stirrer (250 – 350 min^{-1}). The reactor was flushed with nitrogen and while maintaining a slow stream of the gas, the reaction components (ca 0.05 mmol of the ruthenium catalyst or its precursor, 0.2 – 0.6 mmol of a phase-transfer catalyst, eventually a phosphine in excess (up to 0.7 mmol) were introduced. Then the internal standard (undecane or dodecane) was added, followed by the solvents (2.5 ml of chlorobenzene or *o*-xylene and 5 ml of water) and an aqueous 2 M HCOONa solution (2.5 ml). The last component added was the compound to be reduced (1 – 2.5 mmol). The mixture was heated to the reaction temperature (40 – 80 °C) with vigorous stirring. At fixed time intervals the samples of the reaction mixture were withdrawn (max. 0.3 ml) and immediately diluted with the same volume of diethyl ether.

Analysis and Data Treatment

The samples worked up as mentioned above were analyzed by gas chromatography on the content of the starting carbonyl compound and its reduction product, the corresponding alcohol, using internal standards (undecane for heptanal reduction and dodecane for the reduction of cyclohexanone) under the following conditions: Chrom 5a Chromatograph (Laboratorni pristroje, Prague) equipped with a flame ionization detector and a 3.6 m-long column (3 mm i.d.) packed with 10% silicone elastomer OV-17 on Chromosorb W-DMCS. Temperature program was run from 110 to 200 °C with the gradient 6 °C per min, nitrogen as a carrier gas. The contents of the above compounds in the samples were obtained with the use of calibration graphs relating chromatographic responses of the components to those of the internal standard.

Data obtained in the form of time–concentration dependence were treated using a simple model of the first-order reaction in both the catalyst and the substrate. The rate constants so obtained were taken as a measure of the efficiency of the catalyst in dependence on its type, method of its formation and reaction conditions. A set of time and concentration data was solved numerically as a pseudo-first-order reaction (Eq. (*1*)), [S] denotes substrate concentration). The constant k' was further divided by the initial catalyst concentration (Eq. (*2*)) to eliminate the influence of this term.

$$-\,\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k'\,[\mathrm{S}] \tag{1}$$

$$-\,\mathrm{d}[\mathrm{S}]/\mathrm{d}t = k\,[\mathrm{cat}_0]\,[\mathrm{S}] \tag{2}$$

The so obtained k values are presented in Tables I – III. The above kinetic scheme was obeyed in the case of optimum reaction conditions to substrate conversions exceeding 90 per cent. The k values were determined with the relative error 7 to 13 per cent. In two cases (catalyst *I* and *IV*), the temperature dependence of rate data was measured with cyclohexanone and used to estimate activation parameters of the reduction (see Table II).

RESULTS AND DISCUSSION

Reduction Catalyzed by Ruthenium Complexes I – IV

It is well known that reactions between reactants present each in one of the two immiscible phases are besides chemical factors (i.e. the structure of reactants and catalysts, reaction conditions) affected also by mass transport between these phases. In the case of the hydrogen transfer reduction under study, these factors were already thoroughly examined by other authors[19] and demonstrated on an example of the reduction of *p*-tolualdehyde (Eq. (*A*)) in the presence of a methyltrioctylammonium salt (preferentially X = $HCOO^{(-)}$) as a phase transfer catalyst.

$$p\text{-}CH_3C_6H_5CHO_{(org)} + HCOONa_{(aq)} \xrightarrow[\text{Ru cat., } H_2O/C_6H_5Cl]{CH_3(C_8H_{15})_3N^{(+)}X^{(-)}} p\text{-}CH_3C_6H_5CH_2OH_{(org)} + NaHCO_{3(aq)} \qquad (A)$$

TABLE I

Reduction of carbonyl compounds with aqueous sodium formate catalyzed by Ru(II) complexes *I* – *IV* (1.8 mmol substrate, 0.045 mmol Ru catalyst, 2.5 ml chlorobenzene, 2.5 ml aqueous 2 M HCOONa solution, 5 ml water, 0.18 cetylpyridinium bromide, 0.15 ml internal chromatographic standard)

Ru complex	Free ligand, mmol	$k \cdot 10^2$, l mol^{-1} s^{-1}	
		cyclohexanone[a]	heptanal[b]
I	0	1.4	13
	0.85	0.8	48
II[c]	0	0.4	0.6
III[c]	0	0.7	0.8
IV	0	9.4	3.1
	0.85	9.8	13

At: [a] 50 °C; [b] 60 °; [c] 70 °C.

TABLE II

Temperature dependence of the rate constants *k* of reduction of cyclohexanone with HCOONa catalyzed by ruthenium complexes *I* and *IV* (for reaction conditions see Table I)

t, °C	k^a, l mol^{-1} s^{-1}	
	I	*IV*
60	1.6	9.4
70	4.4	18.5
80	9.8	33.2
E_{act}, kJ mol^{-1}	96.3	61.9

[a] Equation (*2*).

Starting from reported data[19], several reaction parameters were maintained constant to ensure good reproducibility of experimental results: one and the same reactor in all experiments, the same magnetic stirring bar and stirring speed (320 – 350 min^{-1}, above the critical mixing speed[19]), the same volume of the reaction mixture (10 ml) with a constant ratio of both phases (the aqueous to organic phase 3 : 1 v/v).

As the study was aimed at comparison of the catalytic properties of a series of ruthenium(II)-phosphine complexes and interpretation of the results in terms of structure differences, the type of the phase transfer agent (cetylpyridinium bromide was chosen on the basis of preliminary experiments as the most suitable of the compounds tested –

TABLE III

Activity of ruthenium catalysts prepared in situ in two phase reduction of heptanal (1.8 mmol heptanal, 0.045 mmol Ru compound, 0.85 mmol free phosphine, the other conditions as in Table I)

Entry	Phosphine added	k . 10^2 l mol^{-1} s^{-1}[a]	Heptanal conversion, %[b]
	$RuCl_3$. 3 H_2O (method *A*, Experimental)		
1	none	0	0
2	$P(C_6H_5)_3$	0[c]	0[c]
3	$P(C_6H_5)_3$	0.7	9.2
4	$P(C_6H_5)_2CH_2CH_2OCH_3$	0.2[c]	2.8
5	$P(C_6H_5)_2CH_2CH_2OCH_3$	20.4	95.5
6	$P(C_6H_5)_2CH_2CH_2OC_2H_5$	0.9	11.8
7	$P(C_6H_5)_2CH_2CH_2OC_4H_7$	1.1	15.5
8	$P(C_6H_5)_2CH_2CH_2CH_2CH_3$	0.4	5.7
9	$P(i\text{-}C_3H_7)_3$	0.2	3.0
	$RuCl_2[P(C_6H_5)_3]_3$ (method *B*, Experimental)		
10	none	0.8[c]	8.5[c]
11	$P(C_6H_5)_3$	0.9[c]	10[c]
12	$P(C_6H_5)_3$	13	80.7
13	$P(C_6H_5)_2CH_2CH_2OCH_3$	1.7[c]	22[c]
	$RuCl_2[P(C_6H_5)_2CH_2CH_2OCH_3]_2$ (method *B*, Experimental)		
14	none	1.1[c]	11.5
15	none	13.3	93.5
16	$P(C_6H_5)_2CH_2CH_2OCH_3$	1.8[c]	30.3[c]
17	$P(C_6H_5)_2CH_2CH_2OCH_3$	48	99.8

[a] Equation (*2*). [b] The reaction time 1 h, determined by gas chromatography (see Analysis and Data Treatment in Experimental). Other products than heptanol were not detected. [c] The reaction was carried out in the absence of the phase transfer catalyst (cetylpyridinium bromide).

see Experimental) and its narrow concentration range (given by its constant ratio with respect to the Ru catalyst – see Procedure in Experimental) were maintained the same through all the experiments. Chlorobenzene was chosen as the solvent based on preparatory cyclohexanone reduction in the presence of the ruthenium ether-phosphine complex *I*. In nonchlorinated aromatic hydrocarbons such as xylene or toluene the reaction proceeded at distinctly slower rate. The same situation was already reported[19] for the reaction (*A*) and ascribed to the higher dielectric constant of the former solvent.

To characterize the activity of the catalysts quantitatively, we determined first the kinetics of the reaction (for procedure and treatment of data see Experimental). We have found that the reduction is first order in the catalyst, as documented by the following dependence of k (Eq. (*1*)) on $[I]_0$ for cyclohexanone (1.8 mmol) (chlorobenzene (2.5 ml), water (5 ml), 2 M HCOONa (2 ml), cetylpyridinium bromide (0.18 mmol), 50 °C).

$k \,.\, 10^3$, min^{-1}	3.2	5.2	7.3
$[I]_0$, mmol l^{-1}	9.7	15.3	19.5

As shown in Fig. 1, the reaction followed well the first-order kinetics in the substrate for at least two half times and that both for the aldehyde (curve *1*) and the ketone (curve *2*). These results confirmed Eq. (*1*) and allowed to describe the efficiency of the catalyst by the rate constant k (Eq. (*2*), cf. Experimental).

The k values obtained under comparable conditions for the ruthenium(II) complexes *I* – *IV* presented in Table I show that of the three ether-phosphine complexes tested, only that having aliphatic straight chain P,O group (*I*) exerts activity comparable to the Ru-phosphine complex *IV*. However, by contrast to $RuCl_2[P(C_6H_5)_3]_3$ which does not differentiate much between both reduced substrates (especially in the presence of the excess free ligand, cf. the last row of Table I), the Ru-ether phosphine complex *I* shows at least by one order of magnitude greater activity (measured by k values, cf. the first

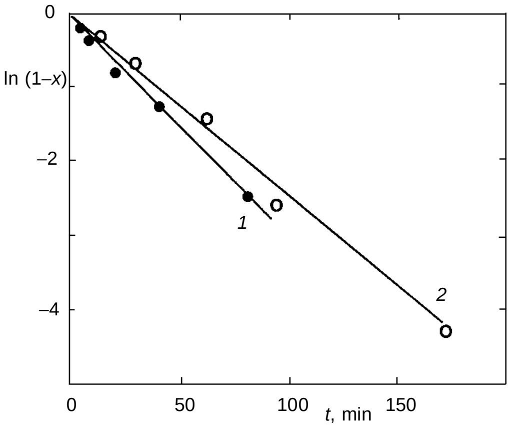

FIG.1
Plot of ln (1 − x) vs time for the biphase reduction of heptanal (50 °C, curve *1*) and cyclohexanone (60 °C, curve *2*) with sodium formate catalyzed by $RuCl_2[P(C_6H_5)_2CH_2CH_2OCH_3]_2$ (for conditions see Table I)

row in Table I) in the aldehyde than ketone reduction. At the same time, in the former reduction it is also distinctly more efficient than the ruthenium-triphenylphosphine complex *IV* (compare $k = 48 \cdot 10^{-2}$ and $13 \cdot 10^{-2}$ for *I* and *IV*, respectively, Table I).

The favourable effect of the added free phosphine on both catalysts *I* and *IV* is specific and limited to the aldehyde reduction. Although it has not so far been noticed for the ruthenium catalysts, it was found[18] in an analogous reduction of *p*-tolualdehyde catalyzed with some rhodium-triphenylphosphine complexes (Wilkinson catalyst and $RhCl(CO)[P(C_6H_5)_3]_2$). It was attributed to stabilization of the complexes towards their reduction to the inactive free metal by added phosphines. However, such an effect cannot be the only reason of the enhanced activity of both ruthenium complexes mentioned as neither of them was visibly reduced to the metal at the beginning or during the reaction. According to our opinion it reflects rather an increased concentration of the catalytically active species or their structure difference leading to the rate enhancing effect. In any case, these processes should take place fast at the beginning of the reaction as they do not change its kinetics (do not cause any significant deviation from the first-order reaction).

The first-order kinetics followed to the late stages of the reduction of both substrates further indicates that its rate is not product-dependent. Furthermore, within the region of the initial substrate concentrations chosen ($1 - 2.5 \cdot 10^{-2}$ mol l^{-1}, see Procedure in Experimental) the concentration effect was that predicted by the first-order kinetics (for the rate retarding effect of the substrate when used in greater amounts cf. ref.[19]).

Nevertheless, as the rate constants *k* used here to characterize the efficiency of the studied catalysts include in the phase transfer processes also the mass transfer contribution (for detailed discussion see ref.[19]), it was of interest to compare the behaviour of the above catalysts *I* and *IV* on the basis of activation data. The temperature dependence of k's for the reduction of cyclohexanone (Table II) gave the following activation energies: E_{act} 96.3 kJ mol^{-1} (23.0 kcal mol^{-1}) for ruthenium ether-phosphine complex *I* and 61.9 kJ mol^{-1} (14.8 kcal mol^{-1}) for ruthenium-triphenylphosphine complex *IV*. In both cases their magnitude speaks for the chemical control of the reduction (chemically controlled hydrogen transfer hydrogenations are reported[25] to have activation energies 20 – 25 kcal mol^{-1} while typical diffusion controlled processes 4 – 5 kcal mol^{-1}, as reported in ref.[19]).

The Effect of Other Phosphine Ligands

The encouranging results obtained with the ruthenium ether-phosphine complex *I* in the reduction of heptanal led us to examine the behaviour of the two other linear chain P,O ligands such as $P(C_6H_5)_2CH_2CH_2OC_2H_5$ and $P(C_6H_5)_2CH_2CH_2OC_4H_7$. However, by contrast to the above complex obtained in high preparative yield[16], all our attempts at preparing analogous Ru(II) complexes containing the above ligands starting from $RuCl_3 \cdot 3\,H_2O$ have failed to give well defined products (instead, red viscous liquids of variable composition were obtained). Similarly also an alternative way found to be successful[16] in preparing the ruthenium-dioxanylphosphine complex *III* and based on the exchange of triphenylphosphine in $RuCl_2[P(C_6H_5)_3]_3$ have not met with success in any of its modifications used.

However, both precursors can be used to form catalysts in situ, using procedures described in detail in Experimental. The results obtained with these systems are summarized in Table III. Several comments can be made concerning these data: (i) the reduction does not proceed with $RhCl_3$ precursor in the absence of phosphine even with the phase transfer catalyst added (entry 1, Table III). (ii) On the other hand, the reduction does not take place when the phosphine is added but without the phase transfer catalyst (entries 2 and 4). When the complexes *I* and *IV* are separately prepared and used as precursors, the reaction pathway not including the phase transfer catalyst becomes appreciable (entries 10 and 14), the more so when the catalyst system is stabilized by the free ligand addition (entries 13 and 16). This effect is less pronounced in the case of the less efficient catalyst (compare entries 10 and 11 for complex *IV*). (iii) Except for the $RuCl_3 + P(C_6H_5)_2CH_2CH_2OCH_3$ system, the other ether-phosphines (entries 5 and 6) were much less efficient, which could be ascribed to their low stability observed also in their separate preparation, as already mentioned. The favourable effect of the O-donor atom in 2-methoxyethyl(diphenyl)phosphine (entry 5) is well illustrated by comparison with the C-analogue of the phosphine, butyl(diphenyl)phosphine (entry 8) which yields the system with markedly lower catalytic activity. (iv) The rather high sensitivity to relatively small structure changes of the ether-phosphines follows from comparison of data for methoxy (entry 5), ethoxy (entry 6, and butoxy (entry 7) derivative. (v) The fact that the system prepared in situ from ruthenium trichloride and the methoxyethylphosphine (entry 5) shows activity higher than the ruthenium-triphenylphosphine complex *IV* (entry 12) offers advantage in avoiding the separate synthesis of the catalyst.

CONCLUSIONS

As documented by the results obtained with two model carbonyl compounds, the ruthenium ether-phosphine complex $RuCl_2[P(C_6H_5)_2CH_2CH_2OCH_3]_2$ (*I*) is an efficient catalyst of the hydrogen transfer reduction of aliphatic saturated aldehydes and ketones by sodium formate. In the aldehyde reduction its activity exceeds significantly that of the so far best catalyst[18], $RuCl_2[P(C_6H_5)_3]_3$. The reduction proceeds as the first-order reaction in the catalyst and in the substrate. Based on energetic data, the ketone reduction is an example of chemically controlled phase transfer reaction. The reduction of the aldehyde catalyzed by the ether-phosphine complex proceeds to a significant extent also by the way which does not include participation of the phase transfer catalyst. Of synthetic importance could be the fact that the efficient catalytic system is formed also under reaction conditions from the metal precursor, $RuCl_3 . 3 H_2O$, and the phosphine, by which the separate synthesis of the ruthenium ether-phosphine complex is avoided.

REFERENCES

1. Lindner E., Meyer S., Wegner P., Karle B., Sickinger A., Steger B.: J. Organomet. Chem. *335*, 59 (1987).
2. Okano T., Morimoto K., Konishi H., Kiji J.: Nippon Kagaku Kaishi *1985*, 486.
3. Vilay Sen Reddy V., Whitten J. E., Redmill K. A., Varshney A., Gray G. M.: J. Organomet. Chem. *372*, 207 (1989).
4. Lindner E., Speidel R.: Z. Naturforsch., B *44*, 437 (1989).
5. Okano T., Iwahara M., Suzuki T.: Chem. Lett. *1986*, 1467.
6. Lindner E., Speidel R., Fawzi R., Hiller W.: Chem. Ber. *123*, 2255 (1990).
7. Lindner E., Mayer S.: J. Organomet. Chem. *339*, 193 (1988).
8. Lindner E., Glaser E., Mayer H. A., Wegner P.: J. Organomet. Chem. *398*, 325 (1990).
9. Vilay Sen Reddy V., Varshney A., Gray G. M.: J. Organomet. Chem. *391*, 259 (1990).
10. Lindner E., Schober U., Staengle M.: J. Organomet. Chem. *331*, C13 (1987).
11. Bader A., Lindner E.: Coord. Chem. Rev. *108*, 27 (1991).
12. Okano T., Yamamoto M., Noguchi T., Konishi H., Kiji J.: Chem. Lett. *1982*, 977.
13. Okano T., Moriyama Y., Konishi H., Kiji J.: Chem. Lett. *1986*, 1463.
14. Lindner E., Wang Q., Mayer H. A., Bader A.: Organometallics *12*, 3291 (1993).
15. Esteruelaz M. A., Lopez A. M., Oro L. A., Perez A., Schulz M., Werner H.: Organometallics *12*, l823 (1993).
16. Lindner E., Schober R., Fawzi R., Englert U., Wegner P.: Chem. Ber. *120*, 1621 (1987).
17. Hetflejs J., Svoboda P., Rericha R., Vcelak J.: Unpublished results.
18. Bar R., Sasson Y., Blum J.: J. Mol. Catal. *26*, 327 (1984).
19. Bar R., Bar L. K., Sasson Y., Blum J.: J. Mol. Catal. *33*, 161 (1985).
20. Mc Ewen W. B., Janes A. B., Knapczyk J. W., Kyllingstad V. L., Shian W. I., Shore S., Smith J. H.: J. Am. Chem. Soc. *100*, 7304 (1978).
21. Iwasaki F., Yoshitani K.: Japan. Kokai Tokkyo Koho JP 04 21,646 (92 21,646); Chem. Abstr. *116*, 235077 (1992).
22. Lindner E., Reudeler H., Scheytt C., Mayer H. A., Hiller W., Fawzi R., Wegner P.: Z. Naturforsch., B *39*, 32 (1984).
23. Lindner E., Sickinger A., Wegner P.: J. Organomet. Chem. *312*, C37 (1986).
24. Smirnov V. V., Antonova N. G., Zotov S. B., Kvasniuk-Mudryi F. V., Sitanova N. A.: Zh. Org. Khim. *4*, 1740 (1968).
25. Sasson Y., Blum J.: J. Org. Chem. *40*, 1887 (1975).