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Transformation of Carbinols by $RuCl_2(PPh_3)_3$ and by Some Other Transition-Metal Catalysts[1]

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Several platinoid metal catalysts have been shown to promote reductive coupling, dehydration, disproportionation, and dehydrogenation of diarylcarbinols. Mechanistic studies were performed at 180–210 °C with benzhydrol as substrate and $RuCl_2(PPh_3)_3$ as catalyst. In aromatic hydrocarbon solvents the main process is reductive coupling. In this medium solvated $RuCl_2(PPh_3)_2$ is suggested to be the active catalyst. In dimethyl sulfoxide the starting complex is transformed initially into $RuCl_2(PPh_3)(Me_2SO)_2$ and causes chiefly carbinol dehydrogenation. Ruthenium alkoxides are implied as common reaction intermediates in all four catalyses. Ruthenium hydrides are suggested to take part in the reductive coupling, disproportionation, and dehydrogenation processes. Some aliphatic and primary aromatic alcohols that do not react by themselves in the presence of $RuCl_2(PPh_3)_3$ can both serve as active hydrogen donors and form crossover products in the presence of secondary and tertiary aromatic carbinols.

Transition-metal complexes have been shown to catalyze hydrogen transfer from carbinols to various unsaturated compounds.[2] In the absence of external hydrogen acceptors, however, the carbinols often undergo internal hydrogen-transfer reactions such as dehydration,[3] dehydrogenation,[4] disproportionation, and reductive coupling as noted in our preliminary report of this study.[5]

In this paper we describe a comprehensive account on the intrinsic transformations of some secondary aromatic alcohols by platinoid metal catalysts, including a study on the utility and on the mechanistic features of the catalytic system.

Results

Outline of Catalysis. When a solution of 3×10^{-3} mmol of $RuCl_2(PPh_3)_3$ and 0.5 mmol of benzhydrol in 0.3 mL of 1-methylnaphthalene was heated at 200 °C for 4 h under exclusion of air, the resulting mixture consisted of 24.6 mol %[6] of 1,1,2,2-tetraphenylethane, 25.1 mol %[6] of benzophenone, 1.4 mol %[6] of dibenzhydryl ether, 2.1 mol %[6] of diphenylmethane, water, and 20 mol % of unchanged starting carbinol. Thus, under these conditions reductive coupling (eq 1) is the dominating process (92.3%)

$$3R_2CHOH \rightarrow R_2CHCHR_2 + R_2CO + 2H_2O \qquad (1)$$

while etherification (eq 2), disproportionation (or internal hydrogenolysis) (eq 3), and dehydrogenation (eq 4) can be regarded as side reactions.

$$2R_2CHOH \rightarrow R_2CHOCHR_2 + H_2O \qquad (2)$$

$$2R_2CHOH \rightarrow R_2CH_2 + R_2CO + H_2O \qquad (3)$$

$$R_2CHOH \rightarrow R_2CO + H_2 \qquad (4)$$

Blank experiments in which the ruthenium catalyst was substituted by equimolar quantities of HCl gas or anhydrous $AlCl_3$ gave dibenzhydryl ether as the main product (22–28 mol %) and only traces of 1,1,2,2-tetraphenylethane. This indicates that reaction 1 is not an acid-catalyzed process. It should be noted, however, that the presence of chloride ion is essential for catalysis 1. Thus, while highly purified chloride-free Ru/C has no catalytic activity, commercial 5% Ru/C (3×10^{-3} mmol, which proved to contain some Cl^- as impurity) converted benzhydrol (0.5 mmol) in 0.5 mL of 1-methylnaphthalene at 210 °C after 24 h into a mixture of 13 mol % of 1,1,2,2-tetraphenylethane, 36 mol % of benzophenone, 20 mol % of diphenylmethane, and 0.7 mol % of dibenzhydryl ether in addition to 11 mol % of the starting carbinol. When an equimolar amount of NH_4Cl was added to the heterogeneous ruthenium catalyst, the selectivity increased substantially, and the yields of $[(C_6H_5)_2CH]_2$, $(C_6H_5)_2CO$, $(C_6H_5)_2CH_2$, and $[(C_6H_5)_2CH]_2O$ became 23, 27, 5, and 7 mol %, respectively. These figures resemble the corresponding yields of the $RuCl_2(PPh_3)_3$-catalyzed system operated at 210 °C for 24 h [30 mol % $[(C_6H_5)_2CH]_2$, 32 mol % $(C_6H_5)_2CO$, and 9 mol % $(C_6H_5)_2CH_2$].

Air affects the catalysis in two ways: it lowers the selectivity and causes partial oxidation of both the starting carbinol and the hydrocarbon products.[7] E.g., under the above conditions, but in the presence of 0.8 atm of air, the products are 10.2 mol % of $[(C_6H_5)_2CH]_2$, 10.5 mol % of $[(C_6H_5)_2CH_2]_2O$, and 24.4 mol % of $(C_6H_5)_2CO$. In pure oxygen the yield of benzophenone doubled.

Transformations 1–4 of benzhydrol are catalyzed also by other platinoid metal complexes. However, as shown in Table I, none of the catalysts investigated is as selective as $RuCl_2(PPh_3)_3$.

Para-substituted benzhydrols with electron-attracting groups react similarly to the parent carbinol in 1-methylnaphthalene when $RuCl_2(PPh_3)_3$ is employed as catalyst (Table II). The rates, however, are lower (vide infra). Electron-donating substituents cause an increase in the rate of reductive coupling but lead to reduction in selectivity.

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[1] Part of these studies was presented at the First International Conference on Relations between Homogeneous and Heterogeneous Catalysis, Lyon, Nov 2–6, 1977 (Blum, J. *J. Mol. Catal.* 1977, *3*, 33).

[2] See, e.g.: Beapere, D.; Bauer, P.; Uzan, R. *Can. J. Chem.* 1979, *57*, 218 and references cited therein.

[3] E.g.: Sasson, Y.; Blum, J. *J. Chem. Soc., Chem. Commun.* 1974, 309.

[4] E.g.: Ohkubo, K.; Shoji, T.; Yoshinaga, K. *J. Catal.* 1978, *54*, 166; Ohkubo, K.; Ohgushi, T.; Yoshinaga, K. *J. Coord. Chem.* 1979, *8*, 195 and references cited therein.

[5] Pri-Bar, I.; Buchman, O.; Blum, J. *Tetrahedron Lett.* 1977, 1443.

[6] According to eq 1 and 2, the highest possible yields of tetraphenylethane, of benzophenone, and of dibenzyl ether, are 33, 33, and 50 mol %, respectively.

[7] Cf.: Blum, J.; Becker, J. Y.; Rosenman, H.; Bergmann, E. D. *J. Chem. Soc. B* 1969, 1000.

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Table I. **Transformation of Benzhydrol by Various Homogeneous Catalysts**[a]

	composition of reaction mixture after 4 h, mol %				
catalyst	$(Ph_2CH)_2O$	$(Ph_2CH)_2$	Ph_2CO	Ph_2CH_2	Ph_2CHOH
$[Ru(CO)_3Cl]_2$	35.0	6.5	10.5	7.7	0.0
$RhCl(PPh_3)_3$	17.3	7.9	7.1	0.6	31.2
$RhBr(PPh_3)_3$	24.4	0.9	1.6	0.4	36.0
$PdCl_2(PPh_3)_2$	15.0	2.0	2.0	0.6	54.0
$PtCl_2(PPh_3)_2$	10.7	0.6	0.8	1.5	46.4
$Pt(PPh_3)_4$	7.0	1.0	2.0	0.7	82.0

[a] Reaction conditions: 0.5 mmol of benzhydrol and 3 × 10^{-3} mmol of catalyst in 0.3 mL of 1-methylnaphthalene at 200 °C under exclusion of air.

Table II. Transformation of Some Aromatic Carbinols by $RuCl_2(PPh_3)_3$ under Comparable Conditions[a]

		relative product distribution, mol %				
carbinol	% conversion	diarylmethane	tetraarylethane	ketone	ether	olefin
$C_6H_5CH(OH)CH_3$	50	25		75		
$C_6H_5CH(OH)C_2H_5$	10			100		
$C_6H_5CH(OH)C(CH_3)_3$	5			100		
$(4\text{-}ClC_6H_4)CH(OH)CH_3$	27	18		82		
$(C_6H_5)_2CHOH$	35		42	53	6	
$(4\text{-}ClC_6H_4)_2CHOH$	26	3	40	50	3	
$(4\text{-}CH_3C_6H_4)_2CHOH$	90		41	41	18[b]	
$(4\text{-}CH_3OC_6H_4)_2CHOH$	100		40	44	10[b]	
$C_6H_5CH(OH)CH_2C_6H_5$	20	20		80		
$C_6H_5C(OH)(CH_3)_2$	97			2		92
$(C_6H_5)_2C(OH)CH_3$	100					100
$(C_6H_5)_3COH$	1				100	

[a] Reaction conditions: 0.5 mmol of carbinol and 3 × 10^{-3} mmol of catalyst in 0.3 mL of 1-methylnaphthalene heated for 3 h at 180 °C in an ampule under exclusion of air. [b] At shorter reaction periods the relative amount of ether was larger. Part of the ether has already been converted into tetraarylethane as shown in the text.

Table III. Reaction of Benzhydrol in Various Solvents[a]

		relative product distribution, mol %			
solvent	% conversion	$(PhCH_2)_2O$	$(Ph_2CH)_2$	Ph_2CO	Ph_2CH_2
benzene	95	11	45	41	2
naphthalene	90	3	44	52	1
1-methylnaphthalene	38	6	42	50	2
diphenyl ether	70	6	7	55	31
dimethyl sulfoxide	13	23	5	67	

[a] Reaction system: 0.5 mmol of benzhydrol and 3 × 10^{-3} mmol of $RuCl_2(PPh_3)_3$ in 0.3 mL of solvent heated for 4 h at 180 °C under exclusion of air in a 2-mL ampule.

Alkylarylcarbinols proved to undergo mainly dehydrogenation in 1-methylnaphthalene provided that no oxygen was present in the reaction mixture. Under ambient atmosphere, ether formation prevails as reported previously.[3]

Aromatic tertiary carbinols that have no β-hydrogen atoms (e.g., triphenylcarbinol) are hardly affected by $RuCl_2(PPh_3)_3$ at 180 °C. The only detectable product formed under such conditions is triphenylmethyl ether. On the other hand, tertiary carbinols *with* β-hydrogen atoms (e.g., methyldiphenylcarbinol) are smoothly dehydrated to give olefins (eq 5).

$$RR'CHC(OH)R''Ar \rightarrow RR'C{=}CR''Ar + H_2O \quad (5)$$

Aliphatic alcohols (e.g., *n*-butyl, *sec*-butyl, and isobutyl alcohol) do not react in the presence of the ruthenium catalyst unless a reactive aromatic carbinol is added to the reaction mixture. Such crossover processes will be discussed later.

The nature of the solvent plays an important role in these catalyses. The examples given in Table III indicate that nonpolar aromatic solvents favor reductive coupling of the carbinol (reaction 1) while diphenyl ether assists disproportionation. Reaction 3 prevails also when a "nonreactive" carbinol is used as cosolvent. For example, when 0.1 mmol of dicyclohexylcarbinol is heated for 24 h at 186 °C together with 0.5 mmol of benzhydrol, 3 × 10^{-3} mmol of $RuCl_2(PPh_3)_3$, and 0.3 mL of 1-methylnaphthalene, 37 mol % of $(C_6H_5)_2CH_2$ is formed with only 19 mol % of $[(C_6H_5)_2CH]_2$. The main reaction that takes place in Me_2SO is dehydrogenation (reaction 4). Thus the two systems which lead to highest selectivity, viz., benzhydrol–$RuCl_2(PPh_3)_3$–1-methylnaphthalene and benz-

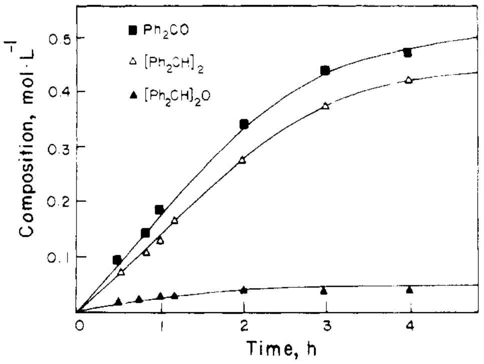

Figure 1. Concentration–time profiles for the formation of 1,1,2,2-tetraphenylethane, benzophenone, and dibenzhydryl ether. Reaction system: 0.5 mmol of benzhydrol and 3 × 10^{-3} mmol of $RuCl_2(PPh_3)_3$ in 0.3 mL of 1-methylnaphthalene at 200 °C.

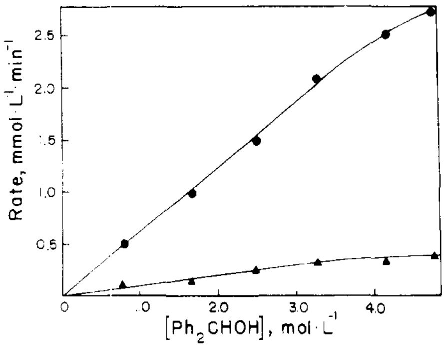

Figure 2. Dependence of initial rates of $[(C_6H_5)_2CH]_2$ (●) and of $[(C_6H_5)_2CH]_2O$ (▲) formation on the concentration of $(C_6H_5)_2CHOH$ in 1-methylnaphthalene. Catalyst concentration 10^{-2} M.

hydrol–$RuCl_2(PPh_3)_3$–Me_2SO were chosen for detailed kinetic studies.

Kinetic Studies in 1-Methylnaphthalene. Figure 1 represents typical reaction curves for the transformation of 1.67 M benzhydrol and 10^{-2} M ruthenium catalyst in 1-methylnaphthalene at 200 °C. It indicates rather complex mechanisms for both reaction 1 and 2. The reductive coupling proved to follow pseudo-zero-order kinetics in the carbinol during the very initial stages of the process with negligible changes in rate. However, these changes become significant when the catalysis advances.

Under the experimental conditions of Figure 1 ether formation does not exceed 10 mol %, and dehydrogenation (shown by the difference in accumulation of Ph_2CO and $(Ph_2CH)_2$ as well as by GLC determination of H_2) is very small. As we will see later, the various transformations of benzhydrol are part of one and the same catalytic cycle in which interaction of the catalyst with the carbinol is common to all four reactions. Therefore, we may regard the initial rate of benzhydrol consumption as the sum of the rates of reactions 1 and 2. A presentation of the logarithm of this rate vs. time indicates that after the first 60 *min of the process, it becomes clearly first order in the* carbinol.

Dependence on Benzhydrol and Catalyst Concentration. Plots of initial rates of reactions 1 and 2 against carbinol concentration are shown in Figure 2.

The rate is first order in benzhydrol as long as the concentration does not exceed 3 M. At higher concentrations the rate dependence decreases. Such plots can be represented by the equation rate = $A[S]/B + [S]$ where [S] is the benzhydrol concentration and A and B are constants. When $[Ph_2CHOH] < 3$ M, $[S] \ll B$ and the rate = $A[S]/B$. The reciprocal function, i.e., 1/initial rate vs. 1/carbinol consumption, is linear and has a very small positive intercept. Thus, the reaction should become very fast in neat carbinol as it proved to be in practice. The linearity of the curves leads to the conclusion that the rate equation does not include any terms in which the power of [S] is greater than 1. ($\text{rate}^{-1} = \alpha/[S] + \beta$; $\alpha = B/A$ and $\beta = A^{-1}$).

Owing to very slow dissolution of $RuCl_2(PPh_3)_3$ in 1-methylnaphthalene, which is associated with structural changes in the complex (vide infra), the dependence on catalyst concentration was studied with the aid of preprepared solutions of the catalyst. Prior to the addition of the carbinol the mixture of $RuCl_2(PPh_3)_3$ and the solvent was heated at 186 °C for 4 h in a sealed tube under exclusion of air. The highest catalyst concentration that could be obtained by this method was 1.5×10^{-2} M. The rate dependence of both reductive coupling and ether formation on catalyst concentration is shown in Figure 3. The curves indicate a linear correlation between the rates and catalyst concentration (at 186 °C) as long as the solution is homogeneous.

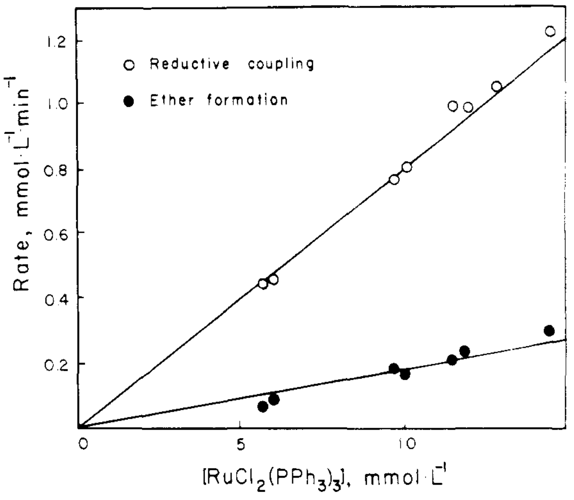

Figure 3. Rate dependence of reactions 1 and 2 on the concentration of the catalyst (prepared by heating of $RuCl_2(PPh_3)_3$ in 1-methylnaphthalene during 4 h) at 186 °C. Initial concentration of $(C_6H_5)_2CHOH$ 1.67 M.

Table IV. Initial Rates of Reductive Coupling and Dehydration of Benzhydrol by Catalysts of Formula $RuCl_2[(4\text{-}XC_6H_4)_3P]_3$ at 186 °C[a]

	initial rate, mmol min⁻¹ L⁻¹	
X	reductive coupling	ether formation
Cl	1.12	0.26
H	1.04	0.19
CH_3	0.96	0.14
OCH_3	0.90	0.13

[a] Reaction system: 1.67 M benzhydrol and 1.1×10^{-2} M catalyst in 1-methylnaphthalene.

Dependence on Electronic Nature of Catalyst. Variations in the electronic nature of the ruthenium catalyst cause small but consistent changes in the rates of reactions 1 and 2. Typical initial rates for benzhydrol transformation by the complexes $RuCl_2[(4\text{-}XC_6H_4)_3P]_3$ where X = Cl, H, CH_3, and OCH_3 are listed in Table IV. The figures indicate that an increase in electron-attracting power of the ligands (i.e., ability to increase the acidity of the metal[8] and to form metal hydrides) parallels the increase in rate. Although the reaction constants of the complex benzhydrol transformation cannot be obtained by simple calculations, it may be assumed that the constants of the rate-controlling steps are proportional to the corresponding *initial velocities. Therefore, the Hammett* plots of the logarithm of the initial rate vs. the σ values of substituents X shown in Figure 4 represent quantitatively the catalyst's electronic effect on reactions 1 and 2.

The small ρ values (+0.22 and +0.60 for reactions 1 and 2, respectively) suggest partial positive charge stabilization on the ruthenium atom in the rate-determining steps.[9]

Dependence on Structure of Carbinol. The influence of the electronic structure of the carbinol was studied by applying para-substituted benzhydrols $(4\text{-}ClC_6H_4)_2CHOH$, $(4\text{-}CH_3C_6H_4)_2CHOH$, and $(4\text{-}CH_3OC_6H_4)_2CHOH$ as substrates. Plots of initial rates vs. carbinol concentration for

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(8) Shriver, D. F. *Acc. Chem. Res.* **1970**, *3*, 231.
(9) Jaffe, H. H. *Chem. Rev.* **1953**, *53*, 191.

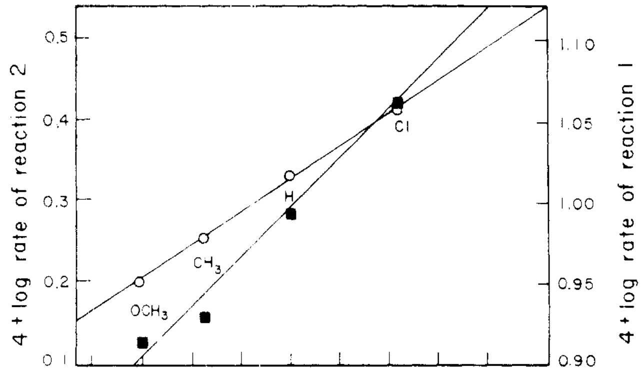

Figure 4. Hammett plots for reactions 1 (●) and 2 (○) with $RuCl_2[4-XC_6H_4)_3P]_3$ catalysts under the conditions given in Table IV. The σ values were taken from: McDaniel, D. H.; Brown, H. C. *J. Org. Chem.* **1958**, *23*, 420.

Table V. Initial Rates of Conversion of Benzhydrols $(4-XC_6H_4)_2CHOH$ by $RuCl_2(PPh_3)_3$ at 186 °C[a]

X	initial rate, mmol min^{-1} L^{-1}		
	consumption of carbinol	formation of tetra-arylethane	formation of ether
Cl	2.0	0.65	0.01
H	3.3	1.04	0.19
CH_3	27	3.0	8.3
OCH_3	125	5.0	55.0

[a] Reaction system: initial concentration of carbinol was 1.67 M and initial concentration of catalyst was 1.1 × 10^{-2} M in 1-methylnaphthalene.

both reactions 1 and 2 proved to be linear between 0.01 and 3.0 M. This suggests identity in reaction mechanisms for the conversion of the substituted and unsubstituted benzhydrols. In both reductive coupling and ether formation the rates increase significantly while the electron-attracting ability of the substituent is lowered. Examples of initial rates for transformation of 1.67 M solutions of carbinols are listed in Table V. The initial rates for $(4-CH_3C_6H_4)_2CHOH$ and $(4-CH_3OC_6H_4)_2CHOH$ had to be taken from very short reaction periods (<5 min), since after a while the recorded rates of these two compounds start to reflect on the combined rates of the dependent reactions 1, 2, and 6.

$$(Ar_2CH)_2O + H_2O \rightarrow (Ar_2CH)_2CHOH \qquad (6)$$

The $RuCl_2(PPh_3)_3$-catalyzed ether decomposition shown in eq 6 proved to be negligible for $[(4-ClC_6H_4)_2CH]_2O$, slow for dibenzhydryl ether (<10% after 8 h at 186 °C), but of considerable significance for the ethers with electron-donating substituents (see, e.g., Figure 5). It should be noted, however, that this catalytic ether decomposition does not involve a dismutation reaction[10] (eq 7) as evidenced by the absence of diarylethanes under our experimental conditions.

$$(Ar_2CH)_2O \rightarrow Ar_2CO + Ar_2CH_2 \qquad (7)$$

From the Hammett plots of the logarithm of the rate vs. the σ of benzhydrol substituents, the ρ values for reactions 1 and 2 were calculated to be −2.2 and −6.4, respectively. These significantly negative values suggest high electron densities at the site of reaction in the activated complex. The opposite signs of ρ for the substituent effects of catalyst and of substrate indicate that the carbinol acts in the rate-determining step as a nucleophile and the ruthenium complex as an electrophile.

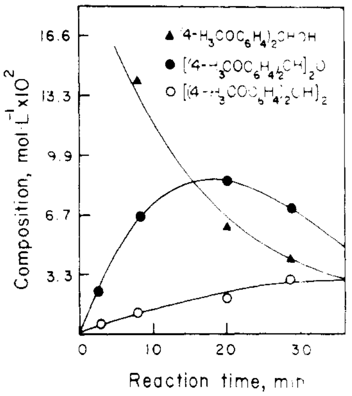

Figure 5. Concentration–time profiles for the reactant and products in $RuCl_2(PPh_3)_3$-catalyzed transformation of $(4-CH_3O-C_6H_4)_2CHOH$. Reaction system: 0.33 M carbinol and 1.1 × 10^{-2} M catalyst in 1-methylnaphthalene at 186 °C.

The influence of steric effects was studied by utilizing (a) dibenzo[*a*,*d*]cyclohepten-5-ol, (b) 10,11-dihydrodibenzo[*a*,*d*]cyclohepten-5-ol, (c) benzhydrol, (d) 2,2′-dimethylbenzhydrol, and (e) fluoren-9-ol as substrates. The accessibility of the OH-attached carbon atom by the ruthenium catalyst decreases in this series of alcohols in going from a to d. Molecular models indicate that although the aromatic rings of benzhydrol can rotate freely over an angle of 180°, only that configuration in which the rings are perpendicular will permit smooth attack of the reacting ruthenium complex at the C–OH carbon atom.[11] Serious shielding of this atom is encountered when methyl groups are introduced in the ortho position in benzhydrol (i.e., as in 2,2′-dimethylbenzhydrol). However, when these groups are linked as in 10,11-dihydrodibenzo[*a*,*d*]cyclohepten-5-ol, the steric interference around the OH group and the OH-attached carbon decreases. The small steric effect associated with the bridge hydrogens (axial configuration) of the latter compound can be removed completely by substitution of the CH_2CH_2 bridge by an ethylenic linkage. In fluoren-9-ol the OH group stays clear above the plain of the aromatic rings. However, the C_9 carbon is totally hindered and inaccessible to the bulky ruthenium catalyst.

Table VI shows that the rate of reductive coupling of carbinols a–d is in perfect correlation with the steric hindrance around the C–OH carbon.

Similar steric effects associated with $RuCl_2(PPh_3)_3$-catalyzed hydrogen transfer from 2-propanol to hindered cyclic ketones have already been reported in the literature.[12]

In contrast to the reductive coupling by bulky $RuCl_2(PPh_3)_3$, the conversion of carbinols a–d by triphenylphosphine-free Ru/C/Cl$^-$ catalyst is hardly influenced by the geometry of the alcohol, and the five compounds react, as expected, at nearly the same rate.

Kinetic Isotope Effect. The dehydration and reductive coupling of $(C_6H_5)_2CHOH$ and of $(C_6H_5)_2CDOD$ were compared at various carbinol concentrations between 0.5 and 5 M. For example, at 186 °C, 1.67 M carbinol, and 1.1 × 10^{-2} M $RuCl_2(PPh_3)_3$, the corresponding rates of dehydration of deuterated and nondeuterated benzhydrol

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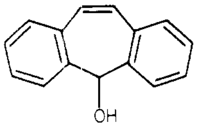
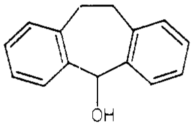
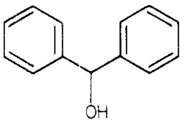
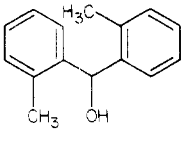
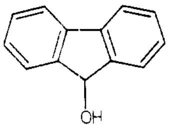
[10] Burton, H.; Cheesman, G. W. H. *J. Chem. Soc.* **1953**, 986.

[11] We assume that the reacting ruthenium catalyst has a square-pyramidal geometry in solution similar to that of $RuCl_2(PPh_3)_3$ (see: La-Placa, S. J.; Ibers, J. A. *Inorg. Chem.* **1965**, *4*, 778; ref 16b).

[12] (a) Sharf, V. Z.; Freidin, L. K.; Krutii, V. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1973**, *22*, 2207. (b) Krutii, V. N.; Chelmakova, S. A.; Gurovets, A. S.; Vasina, T. V.; Furman, D. B.; Sharf, V. Z.; Liberman, A. L. *Ibid.* **1975**, *24*, 1019.

Table VI. Rate of Reductive Coupling of Various Aromatic Carbinols[a]

carbinol	initial rate, mmol L^{-1} min^{-1}
	43.0
	18.5
	1.04
	0.8
	0.0^b

[a] Reaction conditions: 1.67 M carbinol and 1.1 × 10^{-2} M $RuCl_2(PPh_3)_3$ in 0.3 mL of 1-methylnaphthalene at 186 °C. [b] Although no reductive coupling was noted, this carbinol underwent dehydrogenation at a rate of 2.0 mmol L^{-1} min^{-1}.

were 0.15 and 0.19 mmol L^{-1} min^{-1}. The rates of reductive coupling were 0.84 and 1.04, respectively. This secondary isotope effect ($rate_H/rate_D$ = 1.25 ± 0.15 for both reactions) clearly rules out hydride transfer[13] in the rate-determining steps of reactions 1 and 2. A kinetic isotope effect of such magnitude has been observed in processes in which a benzhydryl carbocation is a rate-controlling intermediate.[14]

^{31}P NMR Measurements. The behavior of $RuCl_2(PPh_3)_3$ in polar and nonpolar solvents has been studied by various spectroscopic methods.[15-18] ^{31}P NMR measurements performed at room and subroom temperatures indicate that in nonpolar media the main process is dissociation into PPh_3 and $[RuCl_2(PPh_3)_2]_2$ (eq 8). For example, analysis of the ^{31}P signals at -5.9, 41.7, and 56.0 ppm of an airless 0.1 M $RuCl_2(PPh_3)_3$ solution in C_6D_6 shows that the ruthenium complex is dissociated to an extent of 6.4% at 30 °C. When this solution is heated in a sealed ampule to 190 °C, dissociation exceeds 30%. Prolonged heating in C_6D_6 (but not in 1-methylnaphthalene) causes slow deterioration of the system and separation of PPh_3-free insoluble material.

$$2RuCl_2(PPh_3)_3 \rightleftharpoons [RuCl_2(PPh_3)_2]_2 + 2PPh_3 \quad (8)$$

The dissociation of PPh_3 from $RuCl_2(PPh_3)_3$ increases to 12% at 30 °C when the C_6D_6 solvent is substituted by a 1:1 mixture of C_6D_6 and $(C_6H_5)_2CHOH$. Upon heating of this solution, it stays perfectly homogeneous, and along with the catalytic transformation of the carbinol, new resonance peaks appear at the expense of the $RuCl_2(PPh_3)_3$ phosphorus signal. After 2 h at 190 °C the phosphorus distribution between the ruthenium complexes is 17 atom % in the starting complex (41.6-ppm signal), 2, 3, and 10 atom % in the species that show up at 31.0, 46.2, and 26.7 ppm, respectively (the latter peak does not correspond to Ph_3PO), and 3 atom % in several minor compounds that appear between 20 and 50 ppm. The remaining 65% of the original phosphorus proves to be *free* PPh_3 (-5.9 ppm). This remarkable result shows that while in the absence of carbinol the tris(triphenylphosphine) complex expels just 1 mol of PPh_3, in the presence of benzhydrol nearly 2 mol are extruded.

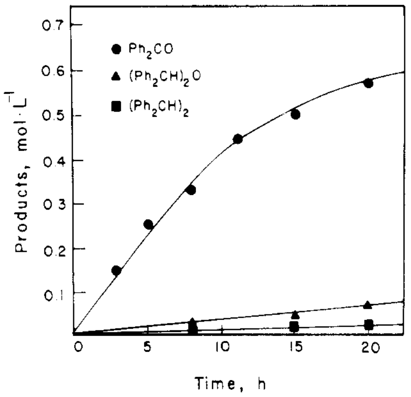


Figure 6. Concentration–time profiles for products formed from benzhydrol and $RuCl_2(PPh_3)_3$ in Me_2SO. Reaction system: 1.67 M carbinol and 1.8 × 10^{-2} M catalyst in 0.3 mL of Me_2SO in a 20-mL ampule under reflux and exclusion of air.

Toward the end of the catalytic process (ca. 3.5 h) the intensity of the -5.9 signal decreases and finally reaches the value of 40% which corresponds to somewhat over 1 mol of PPh_3/mol of Ru. At the same time the peak of the starting material almost disappears completely (only 1.3 mol % remains), and most of the phosphorus concentrates in a compound that has a peak at 24.5 ppm (small peaks at 30.7 and 46.5 ppm remain as well). When now, after consumption of all the benzhydrol, the NMR tube is opened in vacuo and recharged with fresh degassed carbinol followed by heating at 190 °C under exclusion of air, a dramatic increase of the free PPh_3 signal results (up to 58%). Thus it can be concluded that the elimination of two PPh_3 ligands from the ruthenium catalyst is truly associated with the catalytic transformation of benzhydrol.

Some of the ^{31}P signals that are built up during the catalytic process may correspond to species formed by ionic dissociation of $RuCl_2(PPh_3)_3$ (eq 9 and 10) which has been assumed to take place in polar media.[15,17] However, part of the signals must reflect either some other reaction intermediates or ruthenium-containing side products that are formed by reversible reactions from the catalyst.

$$RuCl_2(PPh_3)_3 \rightleftharpoons [RuCl(PPh_3)_3]^+ + Cl^- \quad (9)$$

$$[RuCl(PPh_3)_3]Cl \rightleftharpoons [RuCl(PPh_3)_2]Cl + PPh_3 \quad (10)$$

Kinetic Studies in Me_2SO. Under the conditions of Table III, a solution of benzhydrol in Me_2SO proved to undergo catalytic dehydrogenation accompanied by some dehydration and reductive coupling in rather low yield. When, however, the volume of the reaction vessel was increased by a factor of 10, i.e., a 20-mL ampule was used, catalysis 4 took place almost exclusively (see Figure 6).

As noncatalytic transformations of some alcohols in Me_2SO have been reported,[19,20] it should be noted that

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[13] Swain, C. G.; Wiles, R. A.; Bader, R. F. W. *J. Am. Chem. Soc.* **1961**, *83*, 1945.

[14] Lee, D. G.; van-den-Engh, M. *Can. J. Chem.* **1972**, *50*, 2000, 3129.

[15] James, B. R.; Markham, L. D. *Inorg. Chem.* **1974**, *13*, 97.

[16] (a) Caulton, K. G. *J. Am. Chem. Soc.* **1974**, *96*, 3005. (b) Hoffman, P. R.; Caulton, K. G. *Ibid.* **1975**, *97*, 4221.

[17] Armit, P. W.; Boyd, A. S. F.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1663.

[18] Vriends, R. C. J.; Van Koten, G.; Vrieze, K. *Inorg. Chim. Acta* **1978**, *26*, 429.

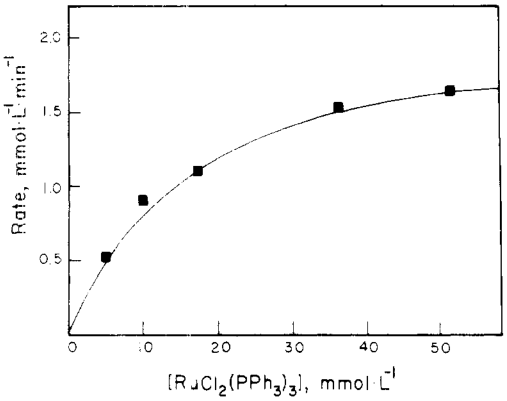

Figure 7. Rate dependence of reaction 4 on the concentration of $RuCl_2(PPh_3)_3$ at 186 °C. Initial benzhydrol concentration in Me_2SO 1.67 M.

Table VII. Effect of Electronic Changes in $RuCl_2[(4\text{-}XC_6H_4)_3P]_3$ on the Rate of Reaction 4[a]

X	initial rate, mmol L^{-1} min^{-1}	X	initial rate, mmol L^{-1} min^{-1}
Cl	0.32	CH_3	1.15
H	0.87	OCH_3	1.57

[a] Reaction conditions: 1.67 M carbinol and 1.1 × 10^{-2} M catalyst in 0.3 mL of Me_2SO in a 20-mL ampule at 186 °C.

under our conditions all blank Ru(II)-free experiments gave absolutely negative results.

In contrast to the kinetics in 1-methylnaphthalene, the transformation of benzhydrol in Me_2SO is pseudo-zero-order in the carbinol during the first 70% of the process. This has been demonstrated both by the linear carbinol concentration–time dependence and by the constant rate observed for benzhydrol–Me_2SO solutions between 1.0 and 3.3 M.

While the dissolution of $RuCl_2(PPh_3)_3$ in 1-methylnaphthalene extended over a long period (vide supra), the complex dissolves instantaneously in Me_2SO. When the catalyst concentration reaches 3 M, yellow $RuCl_2(PPh_3)(Me_2SO)_3$ starts to separate.

The dependence of the initial rate of reaction 4 on catalyst concentration at 186 °C is shown in Figure 7. In a typical experiment in which a 1.67 M benzhydrol solution in Me_2SO was utilized, a linear rate increase was observed for very low catalyst concentration. Above 3 mM the rate increase proved to diverge from linearity and finally reach a maximum and constant value at ~50 mM. A similar rate dependence has already been found and discussed in several other $RuCl_2(PPh_3)_3$-catalyzed hydrogen-transfer processes (see, e.g., ref 21).

The data given in Table VII indicate that an increase in the electronic density on the central ruthenium atom causes a parallel increase in reaction rate. The initial rates can be represented by a Hammett plot (log rate vs. σ) with $\rho = -0.13$.

While both the reductive coupling and dehydration of benzhydrol in 1-methylnaphthalene were associated with secondary deuterium isotope effects, a primary effect was found in the catalytic dehydrogenation in Me_2SO. Under typical conditions (1.67 M carbinol and 1.6 × 10^{-2} M catalyst at 186 °C), for which H–D exchange with the solvent proved negligible, the initial rates of dehydrogenation of $(C_6H_5)_2CHOH$ and of $(C_6H_5)CDOD$ were 1.11 and 0.25 mmol L^{-1} min^{-1}, respectively; $rate_H/rate_D = 4.4$.

Transformation of Mixtures of Carbinols. As noted for some other $RuCl_2(PPh_3)_3$-promoted processes,[21,22] mixtures of two carbinols give, in the presence of the ruthenium catalyst, crossover products. When, e.g., a mixture of 0.24 mmol of benzhydrol and 0.47 mmol of 4,4′-dichlorobenzhydrol was heated for 4 h at 186 °C with a preprepared solution of 3 × 10^{-3} mmol of $RuCl_2(PPh_3)_3$ in 0.3 mL of 1-methylnaphthalene, 24 mol % of 1,1-diphenyl-2,2-bis(4-chlorophenyl)ethane was formed along with the noncrossed products, 1,1,2,2-tetraphenylethane (34 mol %), dibenzhydryl ether (2 mol %), benzophenone (7 mol %), 4,4′-dichlorobenzophenone (27 mol %), and bis(4,4′-dichlorobenzhydryl) ether (1 mol %). Under these conditions 52 and 8% of the chlorinated and nonchlorinated starting carbinols, respectively, were recovered.

This and similar experiments indicate that the carbinol which is least reactive in the reductive coupling and dehydration processes may nevertheless act as a good intermolecular hydrogen donor. Similar behavior has been observed in reactions in which aliphatic alcohols were involved. As mentioned already, aliphatic carbinols do not undergo *internal* hydrogen transfer in the presence of $RuCl_2(PPh_3)_3$ but are capable of participating in the catalytic transformations of active aromatic alcohols such as benzhydrol. They can even be activated, in some cases, just by *mutual* exposure to the ruthenium catalyst under our standard reaction conditions.

The influence of three aliphatic carbinols on the transformation of benzhydrol in 1-methylnaphthalene is given in Table VIII. All three additives increase the conversion of the aromatic carbinol, but, in contrast to the secondary alcohols, *tert*-butyl alcohol is neither consumed in the process nor does it affect the product distribution. 2-Propanol and 2-butanol promote, in addition to reductive coupling, hydrogenolysis of benzhydrol and serve as active hydrogen donors in these processes (eq 11 and 12). This leads, consequently, to a decrease in the transformation of $(C_6H_5)_2CHOH$ into $(C_6H_5)_2CO$ (see Table VIII).

$$RR'CHOH + (C_6H_5)_2CHOH \rightarrow RR'CO + (C_6H_5)_2CH_2 + H_2O \quad (11)$$

$$RR'CHOH + 2(C_6H_5)_2CHOH \rightarrow RR'CO + [(C_6H_5)_2CH]_2 + 2H_2O \quad (12)$$

$$\text{(a) } R = R' = CH_3\text{, (b) } R = CH_3\text{, } R' = C_2H_5$$

Hydrogenolysis and disproportionation of benzhydrol becomes even more pronounced when the added carbinol is benzyl alcohol. When, e.g., an equimolar amount of the latter carbinol (which is unaffected by $RuCl_2(PPh_3)_3$ under our standard conditions) was added to 1.67 M benzhydrol and 1.1 × 10^{-2} M $RuCl_2(PPh_3)_3$ in 1-methylnaphthalene at 200 °C, 22.6% of the primary and 51.5% of the secondary alcohol were consumed within 4 h. The product distribution was 2.8 mol % of 1,1,2,2-tetraphenylethane, 11.4 mol % of diphenylmethane, 13.1 mol % of benzophenone, 3.0 mol % of dibenzhydryl ether, and 16.5 mol % of benzyl benzhydryl ether. In addition to the mixed ether, the benzyl alcohol also gives 5.5% of benzaldehyde and its decarbonylation product and 0.4% of toluene; i.e., 37.8% of the reacted benzhydrol underwent disproportionation and 5.2% hydrogenolysis. Thus, the yields of

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[19] Gillis, B. T.; Beck, P. E. *J. Org. Chem.* **1963**, *28*, 1388.

[20] (a) Traynelis, V. J.; Hergenrother, W.; Hanson, H. T.; Valicenti, J. A. *J. Org. Chem.* **1964**, *29*, 123. (b) Emert, J.; Goldenberg, M.; Chin, G. L.; Valeri, A. *Ibid.* **1977**, *42*, 2012.

[21] Sasson, Y.; Blum, J. *J. Org. Chem.* **1975**, *40*, 1887.

[22] Blum, J.; Zinger, B.; Milstein, D.; Buchman, O. *J. Org. Chem.* **1978**, *43*, 2961.

Table VIII. Effect of Some Aliphatic Carbinols on $RuCl_2(PPh_3)_3$-Catalyzed Transformation of Benzhydrol in 1-Methylnaphthalene[a]

added carbinol	conversion of benzhydrol, %	product distribution, mol % Ph_2CH_2	Ph_2CO	$(Ph_2CH)_2$	$(Ph_2CH)_2O$
none	60	2	44	46	8
tert-butyl alcohol	75	2	48	44	6
2-butanol	71	19	26	53	3
2-propanol	84	10	29	58	4

[a] Reaction conditions: 1.67 M benzhydrol, 5 M aliphatic carbinol, and 1.5×10^{-2} M catalyst in 0.3 mL of solvent heated for 4 h at 186 °C under exclusion of air.

Table IX. Effect of Benzyl Alcohol Concentration on the Main $RuCl_2(PPh_3)_3$-Catalyzed Transformations of Benzhydrol at 210 °C[a]

reaction	relative conversion of $(C_6H_5)_2CHOH$, mol % 2:1[b]	1:1[b]	1:3[b]	1:4[b]
$2(C_6H_5)_2CHOH \rightarrow (C_6H_5)_2CH_2 + (C_6H_5)_2CO + H_2O$	43	31	14	9
$2(C_6H_5)_2CHOH \rightarrow [(C_6H_5)_2CH]_2O + H_2O$	26	10	4	6
$3(C_6H_5)_2CHOH \rightarrow [(C_6H_5)_2CH]_2 + (C_6H_5)_2CO + 2H_2O$	7	7	6	3
$(C_6H_5)_2CHOH + C_6H_5CH_2OH \rightarrow (C_6H_5)_2CHOCH_2C_6H_5 + H_2O$	4	38	67	76
$(C_6H_5)_2CHOH + C_6H_5CH_2OH \rightarrow (C_6H_5)_2CH_2 + C_6H_5CHO + H_2O$	20	14	8	6

[a] Reaction conditions: 1.67 M benzhydrol, 1.1×10^{-2} M catalyst, and 0.3 mL of 1-methylnaphthalene heated for 4 h under exclusion of air. [b] Molar ratio of $(C_6H_5)_2CHOH$ to $C_6H_5CH_2OH$.

reductive coupling and dehydration were suppressed by the additive to 11.4 and 16.0 mol %, respectively. The slight excess of benzaldehyde plus benzene indicates that some dehydrogenation of the benzyl alcohol also occurred. This has been verified by GLC analysis of the H_2 gas in the reaction vessel.

The nature of benzhydrol transformation by $RuCl_2(PPh_3)_3$ is strongly dependent on the *amount* of added benzyl alcohol. In particular, an increase in the concentration of the additive favors formation of the mixed ether (see Table IX).

A similar effect of mutual influence has been observed in the catalytic conversion of benzhydrol and triphenylcarbinol. The tertiary alcohol, which undergoes only very slow dehydration by $RuCl_2(PPh_3)_3$ in 1-methylnaphthalene (see Table II), proved to participate in the transformation of benzhydrol (equimolar quantities) to give, at 186 °C and after 4 h, 16.8 mol % of bis(triphenylmethyl) ether (eq 13),

$$2(C_6H_5)_3COH \rightarrow [(C_6H_5)_3C]_2O + H_2O \quad (13)$$

$$(C_6H_5)_3COH + (C_6H_5)_2CHOH \rightarrow (C_6H_5)_2CHOC(C_6H_5)_3 + H_2O \quad (14)$$

$$(C_6H_5)_3COH + (C_6H_5)_2CHOH \rightarrow (C_6H_5)_3CH + (C_6H_5)_2CO + H_2O \quad (15)$$

10.6 mol % of benzhydryl triphenylmethyl ether (eq 14), and 20.6 mol % of triphenylmethane (hydrogenolysis 15). The corresponding reaction profiles shown in Figure 8 indicate that the asymmetrical ether decomposes and is transferred slowly into two symmetrical ones. The formation of tetraphenylethane, benzophenone, and dibenzhydryl ether from benzhydrol alone (not shown in Figure 8 for the sake of clarity) is not affected by the triphenylcarbinol. The rates of formation of these compounds correspond, however, to the available benzhydrol left after some of it has already been used up in reactions 14 and 15. Unlike benzyl alcohol, $(C_6H_5)_3COH$ does not promote disproportionation of benzhydrol, nor does it initiate any dehydrogenation of the latter compound.

Triphenylcarbinol is also activated by addition of aliphatic carbinols; e.g., the addition of an equimolar amount of 2-butanol to triphenylcarbinol under the standard conditions (1.67 M carbinol and 1.1×10^{-2} M catalyst in 1-methylnaphthalene, 186 °C, 4 h) leads to the formation of 28 mol % of $[(C_6H_5)_3C]_2O$ (eq 13) and to triphenylmethane and 2-butanone (36 mol % of each; eq 16).

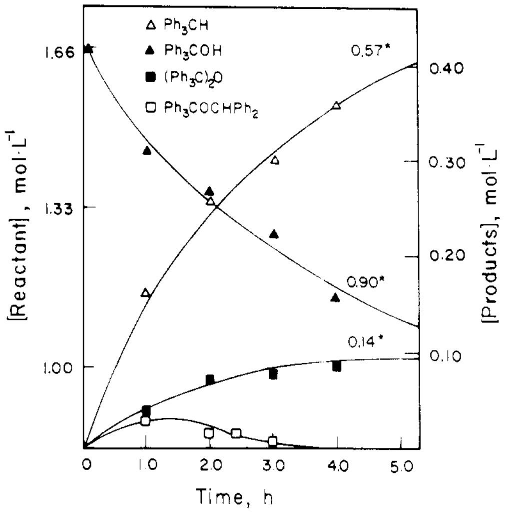

Figure 8. Reaction profiles for transformation products of $(C_6H_5)_3COH$ (1.67 M) in the presence of $RuCl_2(PPh_3)_3$ (1.2×10^{-2} M), benzhydrol (1.67 M), and 1-methylnaphthalene (0.3 mL) at 186 °C. The asterisk indicates the concentration (mol L^{-1}) after 24 h.

$$(C_6H_5)_3COH + CH_3CH(OH)C_2H_5 \rightarrow (C_6H_5)_3CH + CH_3(CO)C_2H_5 + H_2O \quad (16)$$

Discussion

Following the mechanisms suggested for some other $RuCl_2(PPh_3)_3$-promoted reactions (see, e.g., ref 21), we assume the existence of the following steps in our catalytic processes.

Activation of the Catalyst. In the early literature[23-25] it was suggested that $RuCl_2(PPh_3)_3$ is activated by disso-

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[23] Evanson, D.; Osborn, J. A.; Jardine, F. H.; Wilkinson, G. *Nature (London)* **1966**, *208*, 1203.

[24] Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 945.

[25] James, B. R. *Inorg. Chim. Acta, Rev.* **1970**, *4*, 73.

[26] Typically, addition of 0.2 mmol of PPh_3 to 3×10^{-3} mmol of $RuCl_2(PPh_3)_3$ led to 20% retardation in the rates of reductive coupling and dehydration of benzhydrol.

ciation according to eq 17. Recently, such formation of

$$\mathrm{RuCl_2(PPh_3)_3} \xrightleftharpoons{\text{solv}} \mathrm{RuCl_2(PPh_3)_2(solv) + PPh_3} \qquad (17)$$

monomeric $\mathrm{RuCl_2(PPh_3)_2}$ has been questioned, and, instead, dissociation 8 was shown to take place.[16-18] Yet, as $\mathrm{[RuCl_2(PPh_3)_2]_2}$ in 1-methylnaphthalene solution proved (by ^{31}P NMR) to disappear upon heating of the mixture to 190 °C and reappear on cooling, it may be assumed that under our conditions the dimeric complex is transformed into solvated $\mathrm{RuCl_2(PPh_3)_2}$ either by dissociation 18 or by reaction 19.

$$\mathrm{[RuCl_2(PPh_3)_2]_2} \xrightarrow{\text{solv}} \mathrm{2RuCl_2(PPh_3)_2(solv)} \qquad (18)$$

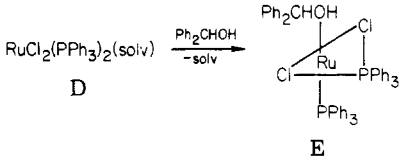
$$\mathrm{[RuCl_2(PPh_3)_2]_2 + PPh_3} \xrightleftharpoons{\text{solv}} \mathrm{RuCl_2(PPh_3)_3 + RuCl_2(PPh_3)_2(solv)} \qquad (19)$$

A possibility that undissociated $\mathrm{RuCl_2(PPh_3)_3}$ takes part in the catalytic process (e.g., in steps A → B → C) is highly

$$\underset{\mathrm{A}}{\mathrm{RuCl_2(PPh_3)_3}} \xrightarrow{\mathrm{H^+}} \underset{\mathrm{B}}{\mathrm{[HRuCl_2(PPh_3)_3]^+}} \xrightarrow[\mathrm{-PPh_3}]{\mathrm{Ph_2CHO^-}} \underset{\mathrm{C}}{\mathrm{HRuCl_2(OCHPh_2)(PPh_3)_2}}$$

improbable because (a) dissociation of A is nearly 100% at 190 °C in dilute (~10^{-2} M) solutions of 1-methylnaphthalene and (b) both the observed *secondary* isotope effect and the electronic effect of the catalyst (Table IV) contradict the expectations for a slow transformation of A to C. (Fast addition of the carbinol can, of course, be ruled out on account of the first-order kinetics in carbinol.)

Activation and Transformation of the Carbinol. Since Ru(II)-catalyzed transformation of benzhydrol in 1-methylnaphthalene is first order both in the carbinol and in the catalyst, it is probable that interaction of the substrate and the activated catalyst is rate controlling. A free-radical pathway[27] can be ruled out in the light of the following observations: (i) neither addition of a free radical scavanger (2,5-di-*tert*-buylhydroquinone) nor of a free-radical initiator [α,α-azobis(isobutyronitrile)] affects the reaction rates; (ii) there exists the Hammett correlation between the electronic nature, both of the catalyst and substrate, and the rate of benzhydrol transformation; (iii) the catalyses depend strongly on the polarity of the solvent. On the other hand, data from Tables IV and V do not support also a mechanism of oxidative addition[21] of the carbinol to the ruthenium complex. Thus, a slow *nonoxidative addition* (D → E) seems more likely. Such a mechanism is in agreement with the kinetic measurements, with the observed rate being increased by electron-donating ligands, and with the absence of a primary kinetic isotope effect. In addition, it explains the sensitivity to structural factors in the substrate, provided that solvated $\mathrm{RuCl_2(PPh_3)_2}$ retains the square-pyramidal geometry of undissociated $\mathrm{RuCl_2(PPh_3)_3}$.[11,28]



As ^{31}P NMR measurements indicate the elimination of a second $\mathrm{PPh_3}$ ligand in course of the catalysis, it can be assumed that transformation E → F is the following step.[29]

$$\mathrm{E} \xrightarrow{\mathrm{-PPh_3,\,-HCl}} \underset{\mathrm{F}}{\mathrm{RuCl(OCHPh_2)(PPh_3)(solv)}}$$

In fact, structural models show that the van der Waals radii of the chlorine and hydroxyl hydrogen atoms of E overlap sufficiently to induce chemical interaction.

By analogy to previous studies in which ruthenium alkoxides were involved, partial rearrangement of F into G, followed by decomposition into benzophenone and hydride H, is likely to take place. By virtue of the small kinetic

$$\mathrm{F} \rightleftharpoons \underset{\mathrm{G}}{\mathrm{HRu(O{=}CPh_2)Cl(PPh_3)(solv)}} \xrightarrow{\mathrm{-Ph_2CO}} \underset{\mathrm{H}}{\mathrm{HRuCl(PPh_3)(solv)}}$$

isotope effect and of the observed electronic effect, both formation and decomposition of G can be regarded as fast processes. Reaction G → H must be irreversible as evidenced by the absence of any change in rate upon addition of free benzophenone or dianisyl ketone to the reaction mixture.

The reaction of F with the previously liberated HCl and $\mathrm{PPh_3}$ would lead to reformation of benzhydrol:

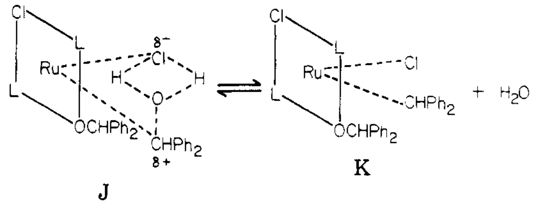
$$\mathrm{F} \xrightarrow[\mathrm{-solv}]{\mathrm{HCl,\,PPh_3}} \underset{\mathrm{I}}{\mathrm{HRu(OCHPh_2)Cl_2(PPh_3)_2}} \xrightarrow[\mathrm{solv}]{\mathrm{-Ph_2CHOH}} \mathrm{D}$$

As reaction I → D is irreversible (vide supra), this addition of anhydrous HCl should bring about serious regression in benzhydrol transformation. However, as the HCl is likely to be hydrated (water is eliminated in processes 1–3), this interaction becomes less significant, and the main catalytic process proceeds smoothly. It is thus understandable why water added to the reaction mixture is associated with an *increase* in the rate of benzhydrol consumption; e.g., addition of 14 mmol of $\mathrm{H_2O}$ to the reaction mixture under the conditions of Table IV increases the rate by a factor of 4. However, HCl is essential for catalyses 1 and 2, and in contrast to some other $\mathrm{RuCl_2(PPh_3)_3}$-catalyzed reactions,[30] its removal by a base (2,5-di-*tert*-butylpyridine) reduces the rate substantially.

Free HCl has been shown to react with the starting carbinol to give "hydrated benzhydryl chloride" (eq 20).

(20)

Such species are known to undergo fast oxidative addition to group 8 metal complexes.[31] A three-centered-type interaction[32] would give intermediate J that leads to the precursor of dibenzhydryl ether, K.



L = $\mathrm{PPh_3}$ or solvent molecule

In the reductive coupling of benzhydrol, complex H is considered to be a key intermediate. Nonoxidative addition of benzhydrol to this complex would give hydride

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[27] E.g.: Pratt, E. F.; Suskind, S. P. *J. Org. Chem.* **1963**, *28*, 638.

[28] Cf. also the structures of $\mathrm{HRuCl(PPh_3)_3}$ and of similar complexes: Skapski, A. C.; Troughton, P. G. H. *Chem. Commun.* **1968**, 1230.

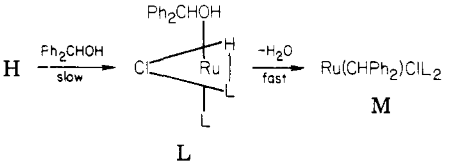
[29] Kaesz, H. D.; Saillant, R. B. *Chem. Rev.* **1972**, *72*, 231 and references cited therein.

[30] E.g.: Sharf, V. Z.; Freidlin, L. K.; Shekoyan, I. S.; Krutii, V. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* (*Engl. Transl.*) **1977**, *26*, 758.

[31] Stille, J. K., Lau, K. S. *Acc. Chem. Res.* **1977**, *10*, 434.

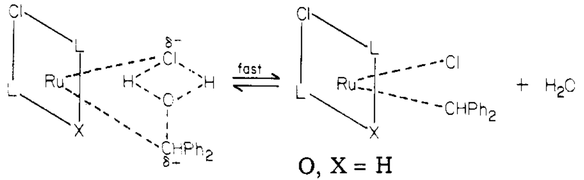
[32] Deeming, A. J. In "Reaction Mechanism in Inorganic Chemistry"; Tobe, M. L. Ed; Butterworths: London, 1972; pp 118–157.

L, which may lead to a benzhydryl complex M. As H has



only very weak acidic properties, transformation H → L must be even slower than D → E, and significant accumulation of a ruthenium hydride should take place. This is, however, not the case. The Fourier transform 270-MHz ^{1}H NMR spectrum indicates that only traces of hydride are found (δ −36.2) under the reaction conditions.

We suggest, therefore, that the formation of benzhydrylruthenium is associated with a *fast* addition of "hydrated benzhydryl chloride" to H. The resulting complex N decomposes then into O.



N, X = H
P, X = CHPh$_2$

O, X = H
Q, X = CHPh$_2$

Elimination of HCl from O gives M that can add once again a second molecule of "hydrated benzhydryl chloride". In analogy to N, intermediate P is expected to decompose into Q from which 1,1,2,2-tetraphenylethane is obtained by reductive elimination. Reforming of complex D in the same step completes the catalytic cycle of reaction 1.

Dependence of the selectivity on the electronic nature of the carbinol can be rationalized in terms of the different modes of decomposition of intermediates N and P and of the ability of the substituents to stabilize diarylmethyl carbonium ions.

Preferential decomposition of N into a dihydride complex and benzhydrol would lead to carbinol dehydrogenation (reaction 4) as a result of H_2 elimination from the dihydride intermediate. The disproportionation reaction (eq 3) becomes important when complex O undergoes reductive elimination to form Ar_2CH_2 and D.

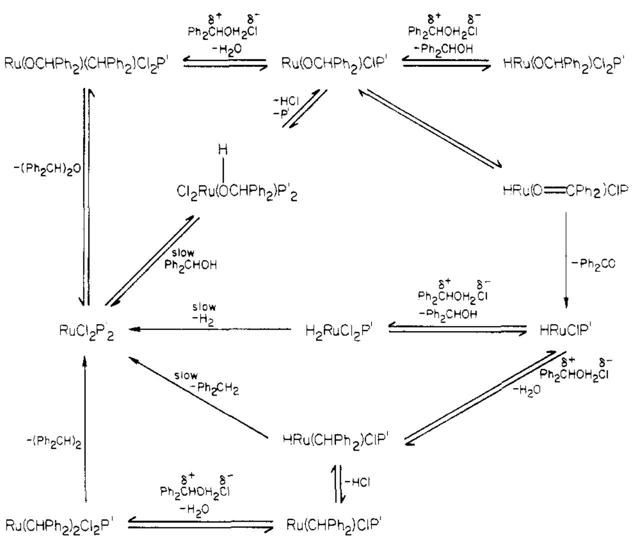
The complete cycle that accounts for the $RuCl_2(PPh_3)_3$-catalyzed transformation reactions of benzhydrol in 1-methylnaphthalene is summarized in Scheme I.

Scheme I can also rationalize the reactions of other carbinols as well as of mixtures of alcohols in 1-methylnaphthalene solution.

Lack of a transferable α-hydrogen atom in triphenylcarbinol prevents the tertiary alcohol from undergoing reactions 1, 3, and 4. It can only form a ruthenium alkoxide in analogy to F. However, the alkoxide from 2-butanol and D, $Ru[OCH(CH_3)(C_2H_5)]ClL_2$ (R), can rearrange into $HRu[O{=}C(CH_3)(C_2H_5)]ClL_2$ (S). Although it has been shown (for an analogous alkoxide)[33] that equilibrium R $\rightleftharpoons$ S is strongly shifted to the left, enough S is formed to give $HRuClL_2$ (H) by loss of 2-butanone. Therefore, the addition of 2-butanol to the reaction mixture of Ph_3COH and $RuCl_2(PPh_3)_3$ leads to substantial hydrogenolysis of the tertiary carbinol (formation of Ph_3CH). The aliphatic alcohol is, however, unable to induce reductive coupling of Ph_3COH due to steric factors.

The effect of benzyl alcohol on the transformation of benzhydrol and of other carbinols can likewise be rationalized by the elements of Scheme I. The alkoxide $Ru(OCH_2Ph)ClL_2$ (T) can add "hydrated benzyl chloride", but since the benzyl cation is less stable than the benzhydryl or triphenylmethine cation, the resulting cyclic intermediate is likely to decompose into $HRu(OCH_2Ph)Cl_2L_2$ (U) in preference to $Ru(OCH_2Ph)(CH_2Ph)Cl_2L_2$ (V) in which a new Ru-C σ bond is formed. This explains the inability of benzyl alcohol to form dibenzyl ether.

Scheme I



[a] P′ = PPh$_3$; solvent molecules involved in the mechanism are not shown.

Mechanism of Benzhydrol Dehydrogenation in Me_2SO. Both GLC and ^{31}P NMR analyses indicate that in a briefly heated 0.03 M solution of $RuCl_2(PPh_3)_3$ in Me_2SO two triphenylphosphine ligands are released (eq 21). The resulting complex W can be isolated upon re-

$$RuCl_2(PPh_3)_3 + 3Me_2SO \rightarrow \underset{W}{RuCl_2(PPh_3)(Me_2SO)_3} + 2PPh_3 \quad (21)$$

cooling of the solution. In more dilute solutions further dissociation takes place (e.g., a 0.015 M $RuCl_2(PPh_3)_3$ preparation releases 85% of the phosphines at 100 °C), and phosphorus-free $RuCl_2(Me_2SO)_4$ (X) is formed on addition to W (eq 22). The activation of the hexacoordinated

$$W + Me_2SO \rightarrow \underset{X}{RuCl_2(Me_2SO)_4} + PPh_3 \quad (22)$$

complex is likely to take place by loss of two Me_2SO ligands followed by recombination of PPh_3 according to eq 23. It

$$X + PPh_3 \rightleftharpoons \underset{Y}{RuCl_2(PPh_3)(Me_2SO)_2} + 2Me_2SO \quad (23)$$

should be noted that conductivity measurements and Cl^- determination indicate that none of the original chlorine ligands is removed from X in the absence of the carbinol substrate.

Support in this mode of activation is found in the changes that occur in the ^{31}P NMR spectrum of $RuCl_2(PPh_3)_3$ in Me_2SO during a temperature increase from 40 to 200 °C. While the signal of free PPh_3 (−2.5 ppm) decreases, two new peaks of metal-bound phosphorus appear. One of the peaks at 31.5 ppm has been shown to correspond to Y (prepared independently[34]), and the second one at 26.4 ppm is assigned to $RuCl_2(PPh_3)_2(Me_2SO)_2$ (Z). (The 26.4-ppm peak appears also in the ^{31}P NMR spec-

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trum of a Me_2SO solution of Y to which excess triphenylphosphine has been added.)

Further support for the intermediacy of Y has been provided by the similar reaction profiles for $RuCl_2(PPh_3)_2$- and $RuCl_2(PPh_3)(Me_2SO)_2$-catalyzed dehydrogenation of benzhydrol in Me_2SO.

The linear concentration–time correlation for benzhydrol dehydrogenation during the first 70% of the process (Figure 6) and the complete independency of the rate on the electronic nature of the carbinol suggest *fast* interaction of the substrate with the active catalyst (eq 24).

$$\mathrm{Y} + \mathrm{Ph_2CHOH} \xrightarrow{\text{fast}} \underset{\mathbf{AA}}{\mathrm{RuCl(OCHPh_2)(PPh_3)(Me_2SO)_2}} + \mathrm{HCl} \qquad (24)$$

In contrast to the methylnaphthalene solution, the HCl liberated in reaction 24 interacts readily with the basic solvent[35] rather than with the carbinol. Therefore, in Me_2SO, catalyses 1 and 2 that involve "hydrated benzhydryl chloride" become unimportant side reactions unless the main course, the dehydrogenation, is suppressed by an increasing hydrogen pressure (provided by introduction of H_2 gas or reduction of the size of the reaction tube).

In analogy to transformation F → H, alkoxide AA can rearrange and liberate benzophenone to give hydride $HRuCl(PPh_3)(Me_2SO)_2$ (BB). Since the rate is decreased by introduction of electron-attracting groups into the phosphine ligands, this step cannot be rate controlling.

The final stages in the catalysis are best described by oxidative addition of HCl to BB (cf. the reverse reaction in *N*,*N*-dimethylacetamide[36]) followed by reductive elimination (eq 25). The last step can be regarded rate determining (i) on account of the primary isotope effect and (ii) by virtue of the observed rate dependence on the electronic structure of the catalyst but not on that of the carbinol.

$$\mathrm{BB} \xrightarrow{\mathrm{HCl}} [\mathrm{H_2RuCl(PPh_3)(Me_2SO)_2}]^+\mathrm{Cl}^- \xrightarrow{-\mathrm{H_2}} \mathrm{Y} \qquad (25)$$

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are not corrected. Infrared and ultraviolet spectra were measured with Perkin-Elmer spectrophotometers, Models 257 and 402, respectively. ^1H NMR spectra were run by using Bruker WH-270 and Varian HA-100D and EM-360 instruments. ^{31}P NMR spectra were taken on Bruker CK-80 and WP-60 spectrometers. Mass spectra were recorded with a Varian MAT-311 spectrometer or were obtained directly from a gas chromatograph using a Varian MAT-111 instrument. Gas chromatography was performed with F&M Model 810 and Hewlett-Packard Model 7620A instruments (equipped with both thermal-conductivity and flame-ionization detectors).

The catalysts $RuCl_2[(C_6H_5)_3P]_3$,[24] $RuCl_2[(4\text{-}ClC_6H_4)_3P]_3$,[37] $RuCl_2[(4\text{-}CH_3C_6H_4)_3P]_3$,[37] $RuCl_2[(4\text{-}CH_3OC_6H_4)_3P]_3$,[37] $HRuCl[(C_6H_5)_3P]_3$,[38] $[RuCl(CO)_3]_2$,[39] $RuCl_2[(C_6H_5)P](Me_2SO)_2$,[33] $(RuCl_2[(C_6H_5)_3P]_2)_2$,[18] $RhCl[(C_6H_5)_3P]_3$,[40] $RhBr[(C_6H_5)_3P]_3$,[40] $PtCl_2[(C_6H_5)_3P]_2$,[41] and $Pt[(C_6H_5)_3P]_4$[41] as well as the reference compounds $[(C_6H_5)_2CH]_2$,[42] $[(4\text{-}ClC_6H_4)_2CH]_2$,[43] $[(4\text{-}FC_6H_4)_2CH]_2$,[44] $[(4\text{-}CH_3C_6H_4)_2CH]_2$,[45] $[(4\text{-}CH_3OC_6H_4)_2CH]_2$,[45] $(4\text{-}ClC_6H_4)_2CH_2$,[46] $(4\text{-}CH_3C_6H_4)_2CH_2$,[46] $(C_6H_5)_2C{=}C(C_6H_5)_2$,[47] $(4\text{-}ClC_6H_4)_2CO$,[48] $(4\text{-}FC_6H_4)_2CO$,[49] $(4\text{-}CH_3C_6H_4)_2CO$,[50] $(4\text{-}CH_3OC_6H_4)_2CO$,[49] $C_6H_5(CO)C(CH_3)_3$,[46] dibenzo[*a*,*d*]cyclohepten-5-one,[51] 10,11-dihydrodibenzo[*a*,*d*]cyclohepten-5-one,[52] $[(C_6H_5)_2CH]_2O$,[53] $[(4\text{-}CH_3C_6H_4)_2CH]_2O$,[54] $C_6H_5CH_2OCH(C_6H_5)_2$,[53] and $(C_6H_5)_2CHOC(C_6H_5)_3$ were prepared as previously described.

Dichloro(triphenylphosphine)tris(dimethyl sulfoxide)ruthenium, $RuCl_2(PPh_3)(Me_2SO)_3$. A solution of 300 mg of $RuCl_2(PPh_3)_3$ in 0.5 mL of Me_2SO was heated under exclusion of oxygen for 1 min at 100 °C. The yellow precipitate that was formed upon cooling was recrystallized from degassed Me_2SO: yield 117 mg (56%); mp 140–143 °C; ^{31}P NMR (Me_2SO-d_6) δ 42.9 (s), 46.5 (s). Anal. Calcd for $C_{24}H_{33}Cl_2O_3PRuS_3$: C, 43.1; H, 4.9; Cl, 10.3; P, 4.6; S, 14.4. Found: C, 42.9; H, 4.8; Cl, 10.3; P, 4.5; S, 14.4.

Most of the noncommercial carbinols were prepared by $NaBH_4$ or $LiAlH_4$ reduction of the corresponding ketones. The following is a typical example.

Methyl(4-methoxyphenyl)carbinol. A solution of 15.0 g of 4-methoxyacetophenone in 250 mL of dry ether was added to a stirred suspension of 2.2 g of $LiAlH_4$ in 250 mL of the same solvent. After 2 h at reflux, the mixture was hydrolyzed with cold aqueous NH_4Cl (10%) and worked up in the usual manner. The residue was distilled at 138–140 °C (15 mm) [lit.[55] 140–141 °C (17 mm)] to yield 13.4 g (88%) of the expected carbinol: ^1H NMR (CCl_4, Me_4Si) δ 1.37 (d, 3, J = 6 Hz), 3.75 (s, 3), 3.77 (s, 1), 4.72 (q, 1, J = 6 Hz), 7.02 (AB q, 4).

α,β-Dideuteriobenzhydrol, $(C_6H_5)_2CDOD$. A mixture of 3.0 g of benzophenone, 10 mL of dioxane, 200 mg of palladium on carbon (10%), and 50 μL of pyridine was treated with D_2 at diminished pressure (~500 mm). After 18 h when the theoretical amount of deuterium had been adsorbed, the catalyst was filtered off, the solvent removed in vacuo, and the residue recrystallized from hexane to yield 2.4 g (80%) of 98% pure benzhydrol-d_2: mp 62–63 °C (lit.[56] mp 65 °C); ^1H NMR (CCl_4, Me_4Si) δ 7.17 (s).

Decadeuteriobenzhydrol, $(C_6D_5)_2CHOH$. A solution of 6 mL of hexadeuteriobenzene (99.8%) in 5 mL of CCl_4 was added to a stirred suspension of $AlCl_3$ in 5 mL of CCl_4 at 5–10 °C. The mixture was stirred for 5 h at 5 °C and then left at 25 °C for a further 16 h. Hydrolysis with water was followed by 1 h at reflux. The mixture was then subjected to steam distillation and the distillate extracted with 30 mL of benzene. The organic layer was dried ($MgSO_4$) and the solvent removed to give 4.0 g (66%) of decadeuteriobenzophenone.

Reduction of the crude ketone in dioxane with H_2 and Pd/C–pyridine catalyst afforded 70% (from crude ketone) of 99% pure $(C_6D_5)_2CHOH$: mp 29–30 °C (from pentane); ^1H NMR (CCl_4, Me_4Si) δ 2.90 (s, 1), 5.60 (s); mass spectrum (70 eV, 24 °C), m/e (relative intensity) 194 ($M^{+\cdot}$, 6), 193 (44), 192 (13), 110 (100), 109 (37), 84 (37), 83 (40), 82 (42), 81 (16), 54 (16).

2,2′-Dimethylbenzhydrol was best obtained by the method of Bertsch et al.[57] from 2-tolualdehyde and 2-tolylmagnesium

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bromide: mp 123 °C (lit.[57] mp 119–120 °C); ^{1}H NMR (CCl_4, Me_4Si) δ 1.85 (s, 1), 282 (s, 6), 5.30 (s, 1), 7.08 (m, 8).

Example of Catalytic Transformation of Benzhydrol by $RuCl_2(PPh_3)_3$ in 1-Methylnaphthalene. (a) Preparation of Catalyst Solution. A 5.0-mL pressure tube (neck length 20 mm) was carefully dried and charged under 1.1 atm of N_2 with 22.3 mg (2.3×10^{-2} mmol) of $RuCl_2(PPh_3)_3$ and 2 mL of 1-methylnaphthalene (freshly vacuum distilled over $LiAlH_4$). The tube was cooled to −78 °C and connected to an efficient vacuum line ($<10^{-2}$ mm) for 2 h. The tube was sealed and immersed at once in a thermostated oil bath at 186 ± 0.05 °C. After 4 h the mixture was cooled and filtered under N_2 through a Millipore filter to yield 1.2 mg of greenish black $[RuCl_2(PPh_3)_3]_x$ of melting point 230 °C dec[21] and a red-brown catalyst solution.

(b) Catalytic Transformation of the Carbinol. A pressure tube of similar dimensions was charged under 1.1 atm of N_2 with 92 mg (0.5 mmol) of benzhydrol and with 0.3 mL of the above catalyst solution (freshly prepared) that contained 3.2 mg (3.3×10^{-3} mmol) of $RuCl_2(PPh_3)_3$. The reaction tube was cooled to −78 °C, connected to a vacuum line for 2 h, sealed, and immersed into a thermostated oil bath at 186 °C. The mixture was perfectly homogeneous during the entire reaction period. After 3 h the solution was cooled and diluted with acetone (AR grade) to a total volume of 10 mL. GLC analysis[58] was carried out (a) with a 40-cm-long column packed with 15% stabilized DEGS on Chromosorb ST-164 operated at 175 °C and (b) with a 60-cm-long column packed with 1% OV-17 on Chromosorb W (60–80 mesh) at 220 °C. The carrier gas for both columns was He at 70 mL/min. The reaction mixture proved to consist of 0.5 mg (1%) of diphenylmethane (column a, retention time 30 s), 10.9 mg (12%) of benzophenone (column a, 140 s), 55.6 mg (60%) of starting material (column a, 340 s), 18.1 mg (22%) of 1,1,2,2-tetraphenylethane (column b, 230 s), and 3.7 mg (4%) of dibenzhydryl ether (column b, 330 s).

For larger scale preparations, the mixtures were separated on silica gel by using petroleum ether as eluent.

The products of the above and further experiments were compared with authentic samples except for the following compounds which were separated by GLC and identified by elementary analysis and spectral properties.

1,2-Dideuterio-1,1,2,2-tetraphenylethane was separated on a 0.6-m-long, 1% OV-17/Chromosorb W column at 220 °C: mp 209–210 °C (from petroleum ether); ^{1}H NMR ($CDCl_3$) δ 1.75 (s); mass spectrum (70 eV, 80 °C), *m/e* (relative intensity) 336 ($M^{+\cdot}$, 0.1), 169 (20), 168 (100), 167 (18), 166 (22), 154 (12). Anal. Calcd for $C_{26}H_{20}D_2$: C, 92.9; H + D, 6.5. Found: C, 92.6; H + D, 6.5.

1,1-Diphenyl-2,2-bis(4-chlorophenyl)ethane was separated on a 0.6-m-long, 1% OV-17/Chromosorb W column at 230 °C: mp 193–195 °C (from petroleum ether); ^{1}H NMR ($CDCl_3$) δ 4.67 (s, 1), 4.69 (s), 7.10 (m, 18); mass spectrum (25 eV, 200 °C), *m/e* (relative intensity) 403 ($M^{+\cdot}$, 0.05), 237 (7), 236 (62), 235 (11), 168 (18), 167 (100), 166 (7), 165 (15). Anal. Calcd for $C_{26}H_{20}Cl_2$: C, 77.4; H, 5.0. Found: C, 77.2; H, 5.2.

Bis(dibenzo[*a*,*d*]cyclohepten-5-yl) was separated on a 0.6-m-long, 1% OV-17/Chromosorb W column at 300 °C: mp 295–298 °C (from MeOH); ^{1}H NMR ($CDCl_3$) δ 4.75 (s, 2), 5.96 (s, 2), 6.64 (s, 2), 7.0–7.5 (m, 16); mass spectrum (25 eV, 200 °C), *m/e* (relative intensity) 382 ($M^{+\cdot}$, 0.5), 192 (2), 192 (18), 191 (100), 190 (1), 189 (3), 164 (2). Anal. Calcd for $C_{30}H_{22}$: C, 94.2; H, 5.7. Found: C, 93.9; H, 5.7.

Bis(10,11-dihydrodibenzo[*a*,*d*]cyclohepten-5-yl) was separated on a 0.6-m-long, 1% OV-17/Chromosorb W column at 260 °C: mp 256–258 °C (from petroleum ether); ^{1}H NMR ($CDCl_3$) δ 3.35 (m, 8), 4.73 (s, 2), 7.0–7.5 (m, 16); mass spectrum (20 eV, 200 °C), *m/e* (relative intensity) 386 ($M^{+\cdot}$, 1), 195 (79), 194 (79), 193 (100), 192 (28), 178 (13), 177 (72), 176 (20), 164 (8), 114 (35). Anal. Calcd for $C_{30}H_{26}$: C, 93.2; H, 6.7. Found: C, 92.9; H, 6.6.

Bis(2-phenylprop-2-yl) ether was separated on a 0.6-m-long, 15% DEGS/Chromosorb W column at 170 °C: ^{1}H NMR ($CDCl_3$) δ 1.29 (s, 12), 7.15 (s, 10); mass spectrum (25 eV, 80 °C), *m/e* (relative intensity) 254 ($M^{+\cdot}$, 34), 121 (63), 119 (100), 118 (92), 117 (48), 105 (95). Anal. Calcd for $C_{18}H_{22}O$: C, 83.6; H, 8.7. Found: C, 83.6; H, 8.6.

Example of Benzhydrol Dehydration by $RuCl_2(PPh_3)_3$ in Me_2SO. Into each of two 20-mL pressure tubes, having break-seal edges, there was introduced under N_2 0.3 mL of a 1.8×10^{-2} M $RuCl_2(PPh_3)_3$ solution in Me_2SO (freshly vacuum distilled over BaO). Then 92 mg (0.5 mmol) of benzhydrol was added; the tubes were cooled with liquid nitrogen, evacuated (10^{-2} mm), sealed, and immersed immediately into a thermostated oil bath at 186 °C. After 8 h the liquid in one tube was analyzed by GLC and found to consist of 18.2 mg (20%) of benzophenone, 70.0 mg (76%) of benzhydrol, 1.8 mg (2%) of dibenzhydryl ether, and 1.0 mg (1.2%) of 1,1,2,2-tetraphenylethane. The second ampule was introduced into a gas trap equipped with a manometer. After the trap has been evacuated, the break-seal edge was broken with a magnet bar, and the liberated gas (0.09 mmol, 18%) was analyzed on a 2-m-long GLC column packed with molecualr sieves 13X and proved to be pure hydrogen.

Kinetic Measurements. Typically, each of 10–20 reaction tubes of exactly the same dimensions were charged in the manner described above, with the same amount of catalyst solution and with the same quantity of carbinol. The sealed ampules were immersed at once into a thermostated oil bath (accuracy ± 0.05 °C). During the first 1 h one ampule was withdrawn each 2–10 min and immediately frozen to −78 °C to await GLC analysis. The initial rate was calculated in each case from at least three experiments.

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Registry No. $(Ph_2CH)_2O$, 574-42-5; $(Ph_2CH)_2$, 632-50-8; Ph_2CO, 119-61-9; Ph_2CH_2, 101-81-5; Ph_2CHOH, 91-01-0; $C_6H_5CH(OH)CH_3$, 98-85-1; $C_6H_5CH(OH)C_2H_5$, 93-54-9; $C_6H_5CH(OH)C(CH_3)_3$, 3835-64-1; $(4\text{-}ClC_6H_4)CH(OH)CH_3$, 3391-10-4; $(4\text{-}ClC_6H_4)_2CHOH$, 90-97-1; $(4\text{-}CH_3C_6H_4)_2CHOH$, 885-77-8; $(4\text{-}CH_3OC_6H_4)_2CHOH$, 728-87-0; $C_6H_5CH(OH)CH_2C_6H_5$, 614-29-9; $C_6H_5C(OH)(CH_3)_2$, 617-94-7; $(C_6H_5)_2C(OH)CH_3$, 599-67-7; $(C_6H_5)_3COH$, 76-84-6; $C_6H_5C_2H_5$, 100-41-4; $(4\text{-}ClC_6H_4)C_2H_5$, 622-98-0; $(4\text{-}ClC_6H_4)_2CH_2$, 101-76-8; $(C_6H_5CH_2)_2$, 103-29-7; $[(4\text{-}ClC_6H_4)_2CH]_2$, 13144-33-7; $[(4\text{-}CH_3C_6H_4)_2CH]_2$, 40673-57-2; $[(4\text{-}CH_3OC_6H_4)_2CH]_2$, 51048-43-2; $PhCOCH_3$, 98-86-2; $PhCOC_2H_5$, 93-55-0; $PhCOC(CH_3)_3$, 938-16-9; $(4\text{-}ClC_6H_4)COCH_3$, 99-91-2; $(4\text{-}ClC_6H_4)_2CO$, 90-98-2; $(4\text{-}CH_3C_6H_4)_2CO$, 611-97-2; $(4\text{-}CH_3OC_6H_4)_2CO$, 90-96-0; $C_6H_5COCH_2C_6H_5$, 451-40-1; $[(4\text{-}ClC_6H_4)_2CH]_2O$, 74562-99-5; $[(4\text{-}CH_3C_6H_4)_2CH]_2O$, 37858-01-8; $[(4\text{-}CH_3OC_6H_4)_2CH]_2O$, 1062-99-3; $[(C_6H_5)_3C]_2O$, 28567-37-5; $C_6H_5C(CH_3){=}CH_2$, 98-83-9; $Ph_2CH{=}CH_2$, 530-48-3; $(C_6H_5)_2CHOCH_2C_6H_5$, 26059-49-4; $[Ru(CO)_3Cl]_2$, 74577-86-9; $RhCl(PPh_3)_3$, 14694-95-2; $RhBr(PPh_3)_3$, 14973-89-8; $PdCl_2(PPh_3)_2$, 13965-03-2; $PtCl_2(PPh_3)_2$, 10199-34-5; $Pt(PPh_3)_4$, 14221-02-4; $RuCl_2(PPh_3)_3$, 15529-49-4; $RuCl_2[(4\text{-}ClC_6H_4)_3P]_3$, 39042-64-3; $RuCl_2[(4\text{-}CH_3C_6H_4)_3P]_3$, 36733-05-8; $RuCl_2[(4\text{-}CH_3OC_6H_4)_3P]_3$, 39114-24-4; $RuCl_2(PPh_3)(Me_2SO)_3$, 74610-49-4; Me_2SO, 67-68-5; dibenzo[*a*,*d*]cyclohepten-5-ol, 10354-00-4; 10,11-dhydrodibenzo[*a*,*d*]cyclohepten-5-ol], 1210-34-0; 2,2′-dimethylbenzhydrol, 2845-91-2; fluoren-9-ol, 1689-64-1; bis(dibenzo[*a*,*d*]cyclohepten-5-yl), 15224-49-4; bis(10,11-dihydrodibenzo[*a*,*d*]cyclohepten-5-yl), 15323-21-4; 1,1,2,2-tetra-*o*-tolylethane, 32313-73-8; bis(fluoren-9-yl), 1530-12-7; *tert*-butyl alcohol, 75-65-0; 2-butanol, 78-92-2; 2-propanol, 67-63-0; benzyl alcohol, 100-51-6; methyl(4-methoxyphenyl)carbinol, 3319-15-1; 4-methoxyacetophenone, 100-06-1; α,β-dideuteriobenzhydrol, 74563-00-1; decadeuteriobenzhydrol, 74563-01-2; hexadeuteriobenzene, 1076-43-3; decadeuteriobenzophenone, 22583-75-1; 2-tolualdehyde, 529-20-4; 2-tolyl bromide, 95-46-5; 1,2-dideuterio-1,1,2,2-tetraphenylethane, 74563-02-3; 1,1-diphenyl-2,2-bis(4-chlorophenyl)ethane, 74563-03-4; bis(2-phenylprop-2-yl) ether, 74563-04-5.

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(58) We have shown that precipitation of the ruthenium compounds by addition of pentane prior to GLC analysis is unnecessary when a Pyrex preinjector was used.