CONVERSION OF LONG-CHAIN TERMINAL ALCOHOLS AND SECONDARY AMINES INTO TERTIARY AMINES USING RUTHENIUM(II) TERTIARY PHOSPHINE COMPLEXES AS HOMOGENEOUS CATALYSTS*

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Abstract—RuCl₂(PPh₃)₃ acts as a homogeneous catalyst for the condensation reaction between long-chain terminal alcohols and secondary amines to give tertiary amines. Supporting evidence is presented for a pathway involving an intermediate aldehyde which undergoes Schiff base formation with the secondary amine. Small amounts of amine side product are formed from catalysed alkyl group transfer reactions between the amines in the solution. A secondary pathway involving decarbonylation of the aldehyde leads to the formation of alkane and RuHCl(CO)(PPh₃)₃. Mechanistic probes are presented and discussed, and the scope of the reaction with secondary alcohols and ketones is presented.

The catalysed synthesis of amines having longchain alkyl groups is of potential commercial value because of the use of these compounds in the production of detergents. A plausible synthetic approach to these compounds involves the condensation reaction between long-chain terminal alcohols and secondary amines [cq. (1)]:

 $Me(CH_2)_{,n}OH + R_2NH \longrightarrow$

$$Me(CH_2)_n NR_2 + H_2O.$$
 (1)

This reaction has been the focus of considerable study for an extended period of time, and numerous heterogeneous catalysts have been developed for accelerating this reaction.² The reaction has received less study as a transformation which can be catalysed under homogeneous conditions, but complexes of ruthenium and other transition metals have been used for similar dehydration reactions.³ An example of such a process is the use of ruthenium triphenylphosphine complexes as homogeneous catalysts for the conversion of ethylene glycol into both monoamines and diamines.⁴ This paper reports our use of ruthenium(II) complexes as homogeneous catalysts for the conversion of longchain terminal alcohols into tertiary amines by the general condensation reaction shown in eq. (1). Alcohols ranging in carbon chain length from 10 to 18 have been used [n = 9, 13, 15, 17 in eq. (1)], and secondary amines have been employed which have methyl, ethyl, 1-propyl and phenyl substituents as the R group in R_2NH .

EXPERIMENTAL

Alcohols and secondary amines were commercial samples and used as supplied. The complexes RuCl₂(PPh₃)₃, RuCl₂(PN)₂, RuCl₂(dppe)₂, RuCl₂ (bipy)₂ and RuCl₂(CO)₂(PPh₃)₂ were synthesized using literature procedures.⁵ Triphenylphosphine (Aldrich) and stannous chloride were commercial samples. The catalytic reactions were carried out in a Parr pressure vessel fitted with a 45 cm³ reaction cup. The reaction cup was heated in an aluminium block, and the reaction mixture stirred by a magnetic stir bar. The cooled reaction mixture was filtered through alumina to remove the ruthenium complexes, and the eluant analysed on a Hewlett-Packard Model 5830 gas chromatographmass spectrometer. Prior to the GC-MS analysis, dodecane (0.75 g, 4.4 mmol) was added to a mixture of the alcohol (10 mmol) and secondary amine (10 mmol). The yield of product tertiary amine was obtained by comparing the peak areas of the reac-

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tant alcohol and product amine with that of the standard dodecane. The relative detector sensitivity for equimolar amounts of terminal alcohol, product amine and dodecane was 1.7:1.3:1 with an accuracy of better than 5%. Our product yields are accurate to approximately 5%, and the selectivity in the majority of cases is greater than 90%. The lowered selectivity in some reactions was reduced because of a catalysed amine scrambling reaction. The yields of other amine products were obtained by GC-MS comparison with dodecane. The complex which was recovered from the reaction at the end of each catalytic run was RuHCl(CO)L(PPh₃)₂, where L is a secondary amine. The complex $RuHCl(CO)(PPh_3)_3$ was prepared by the literature procedure and characterized by a combination of IR, ¹H and ³¹P{¹H} NMR spectroscopy: ν (CO) 2020, 1922, 1903 cm⁻¹; ¹H NMR: δ -7.2 $[^{2}J(PH_{cis}) = 23.7 \text{ Hz}, \ ^{2}J(PH_{trans}) = 104.9 \text{ Hz}];$ ³¹P{¹H} NMR: δ 13.5s, 39.6s [²J(PP) 0 Hz].⁶ Addition of excess diethylamine to a solution of RuHCl(CO)(PPh₃)₃ gave RuHCl(CO)(HNEt₂) (PPh₃)₂, which was characterized by ¹H and ³¹P{¹H} NMR spectroscopy: ¹H NMR: δ $-14.5t \ [^{2}J(PH) = 19.6 \ Hz]; \ ^{31}P\{^{1}H\} \ NMR: \delta$ 47.6s.

RESULTS

When a terminal alcohol, $Me(CH_2)_nOH$ (n = 9, 13, 15, 17), is reacted with a secondary amine, R_2NH (R = Me, Et, 1-Pr, Ph), at 120°C for 2.5 h in the absence of any catalyst, no observable quantity of tertiary amine $Me(CH_2)_n NR_2$ is formed. When the complex $RuCl_2(PPh_3)_3$ (50 µmol) is added to such a reaction mixture containing an alcohol (10 mmol) and a secondary amine (10 mmol) at 120°C, tertiary amine is formed as the product after 2.5 h reaction time (Table 1). After the reaction is complete the only ruthenium complex which can be detected in the solution is RuHCl $(CO)L(PPh_3)_2$, where L is the secondary amine used as the reactant. When the amine L is removed from this solution by evaporation, the complex $RuHCl(CO)(PPh_3)_3$ is formed.⁶ This reaction is readily reversible since we find that the addition of excess secondary amine (L) to RuHCl(CO)(PPh₃)₃ gives $RuHCl(CO)L(PPh_3)_2$ [eq. (2)]:

$$RuHCl(CO)L(PPh_3)_2 \xleftarrow{PPh_3}{L} RuHCl(CO)(PPh_3)_3$$
$$(L = R_2NH).$$
(2)

Terminal	Secondary	Tertiary	Yield	Turnover
alcohol	amine ^b	amine	(%) ^c	number ^d
$C_{10}H_{21}OH$	NHMe ₂	$C_{10}H_{21}NMe_2$	52	104
C ₁₀ H ₂₁ OH	NHEt ₂	$C_{10}H_{21}NEt_2$	24	48
$C_{10}H_{21}OH$	NHPr ₂	$C_{10}H_{21}NPr_2$	26	52
C ₁₀ H ₂₁ OH	NHPh ₂	$C_{10}H_{21}NPh_2$	52	104
C14H29OH	NHMe ₂	$C_{14}H_{29}NMe_2$	75	150
C14H29OH	NHEt ₂	$C_{14}H_{29}NEt_2$	28	56
C14H29OH	NHPr ₂	$C_{14}H_{29}NPr_2$	23	46
C14H29OH	NHPh ₂	$C_{14}H_{29}NPh_2$	50	100
C ₁₆ H ₃₃ OH	NHMe ₂	$C_{16}H_{33}NMe_2$	45	90
C ₁₆ H ₃₃ OH	NHEt ₂	$C_{16}H_{33}NEt_2$	21	42
C ₁₆ H ₃₃ OH	NHPr ₂	$C_{16}H_{33}NPr_2$	24	47
C ₁₆ H ₃₃ OH	NHPh ₂	$C_{16}H_{33}NPh_2$	49	98
C ₁₈ H ₃₇ OH	NHMe ₂	$C_{18}H_{37}NMe_2$	82	164
C ₁₈ H ₃₇ OH	NHEt ₂	$C_{18}H_{37}NEt_{2}$	14	28
C ₁₈ H ₃₇ OH	NHPr ₂	$C_{18}H_{37}NPr_2$	21	42

Table 1. Conversion of terminal alcohols and secondary amines into tertiary amines^a

^{*a*} Reaction conditions: 2.5 h at 120°C with RuCl₂(PPh₃)₃ (0.5%) added.

^b The propyl group is the 1-propyl.

 $^{^{}c}$ Yield of tertiary amine for a reaction containing equal moles of terminal alcohol and secondary amine.

^{*d*} Turnover number based on moles tertiary amine obtained per mole of $RuCl_2(PPh_3)_3$ catalyst.

Catalyst	Temperature (°C)	Yield of $C_{16}H_{33}NPr_2$ (%)
$RuCl_2(PPh_3)_3$	25	0*
$RuCl_2(PPh_3)_3$	70	4 ^{<i>b</i>}
$RuCl_2(PPh_3)_3$	120	24
$RuCl_2(PPh_3)_3 + PPh_3$ (4 moles)	120	51
$RuCl_2(PPh_3)_3 + SnCl_2 \cdot 2H_2O$	120	13
RuCl ₂ (PN) ₂	120	0
$RuCl_2(PN)_2 + PPh_3$ (4 moles)	120	0
RuHCl(CO)(PPh ₃) ₃	120	0
RuCl ₂ (dppe) ₂	120	0
RuCl ₂ (bipy) ₂	120	0
$RuCl_2(CO)_2(PPh_3)_2$	120	5
$\operatorname{RuCl}_{2}(\operatorname{PPh}_{3})_{3}$	160	4 7
$\operatorname{RuCl}_{2}(\operatorname{PPh}_{3})_{3} + \operatorname{PPh}_{3}(4 \text{ moles})$	160	56
RuCl ₂ (PN) ₂	160	15
$RuCl_2(PN)_2 + PPh_3$ (4 moles)	160	72

Table 2. Comparative yield of $C_{16}H_{33}NPr_2$ for different catalytic conditions^{*a*}

^a Reaction time 2.5 h; catalyst concentration 0.5%.

^b Reaction time 30 h.

The complexes RuHCl(CO)L(PPh₃)₂ and RuHCl $(CO)(PPh_3)_3$ are inactive as catalysts for reaction (1), and $RuCl_2(PPh_3)_3$ does not catalyse the reverse reaction. At 120°C, the chelate complexes $RuCl_2(PN)_2$ (PN = o-diphenylphosphino-N,N-dimethylaniline), RuCl₂(dppe)₂, RuCl₂(bipy)₂ and the dicarbonyl complex RuCl₂(CO)₂(PPh₃)₂ are also inactive as homogeneous catalysts for reaction (1). At the higher temperature of 160°C, $RuCl_2(PN)_2$ will catalyse the formation of $C_6H_{33}NPr_2$ from $C_{16}H_{33}OH$ and $NHPr_2$. When the reaction temperature is lowered to 25°C, RuCl₂ $(PPh_3)_3$ is inactive as a catalyst for the formation of $C_{16}H_{33}NPr_2$ over a time period of 30 h, and comparable reaction conditions at 70°C give only a 4% yield of $C_{16}H_{33}NPr_2$ after 30 h (Table 2). Although triphenylphosphine itself is not a catalyst for reaction (1), the addition of 4 moles of triphenylphosphine per mole of $RuCl_2(PPh_3)_3$ to solutions which contain RuCl₂(PPh₃)₃ or RuCl₂(PN)₂ results in increased yields of amine (Table 2). The complex $RuCl_{2}(PN)_{2}$ is not recovered at the end of the catalytic reaction at 160°C under conditions where 4 moles of triphenylphosphine are added. Instead in the ${}^{31}P{}^{1}H$ NMR spectrum we observe a single resonance at δ 25 due to an unidentified complex. The yield of tertiary amine is dependent on both the alcohol and secondary amine. The highest yields are obtained with NHMe₂ and $C_{14}H_{29}OH$ or $C_{18}H_{37}OH$, and the lowest yield with NHEt₂ and

 $C_{18}H_{37}OH$ (Table 1). Secondary and tertiary alcohols do not react; thus in the presence of $RuCl_2(PPh_3)_3$ at 170°C for 2.5 h with dipropylamine, the secondary alcohols 2-propanol, 2octanol, 4-methylcyclohexanol, *t*-butanol and phenol give no tertiary amine products.

The catalytic reaction with primary alcohols and secondary amines exhibits an induction period of approximately 30 min before significant amounts of tertiary amine product are formed. This induction period is reduced when 4 moles of PPh₃ per mole of $RuCl_2(PPh_3)_3$ are added to the solution. Data collected in Table 3 show that the catalysed reaction between $C_{10}H_{21}OH$ and $NHPr_2$ gives increased yields of $C_{10}H_{21}NPr_2$ with added triphenylphosphine at all times after this 15 min induction period. At the early stages of the reaction the ${}^{31}P{}^{1}H$ NMR spectrum shows the presence of $RuCl_2(PPh_3)_3$ (δ 45, 60) as the only phosphorus containing ruthenium complex, whereas at the late stages of the catalysis complete conversion to RuHCl(CO)(NHPr)(PPh₃)₂ (δ 47.8) has occurred. No other complexes are observed in significant amounts. In the presence of added triphenylphosphine we observe the formation of RuHCl $(CO)(NHPr)(PPh_3)_2$ after 90 min, whereas in the absence of added triphenylphosphine we only observe this compound after 180 min.

At the higher temperature of 180°C and the longer reaction time of 10 h we observe the

RuCl₂(PPh₃)₃ catalysed conversion of secondary alcohols into tertiary amines by condensation with primary amines, but not with secondary amines. Thus after the 10 h reaction time we obtain a 43% yield of 4-methylcyclohexylphenylamine from 4methylcyclohexanol and aniline, and a 22% yield of 4-methylcyclohexyl hexylamine from 4-methylcyclohexanol and 1-hexylamine [eq. (3)]. phosphine under a hydrogen pressure of 1300 psig (Table 5).

In some cases the selectivity of the condensation reaction (1) is lowered by a redistribution reaction, whereby the initially formed amine undergoes alkyl group interchange to give a series of different tertiary and secondary amines. This reaction is observed in the reaction between terminal alcohols



With 4-methycyclohexanol and dipropylamine we observe no product amine after 10 h, but after 16 h reaction time the compound 4-methylcyclohexyldipropylamine is formed in 13% yield. Under catalytic conditions at 120°C we observe no tertiary amine formation from dipropylamine and secondary alcohols or ketones. Previous workers have, however, reported that $RuCl_2(PPh_3)_3$ acts as a homogeneous catalyst for the condensation of aniline with *both* secondary and primary alcohols, therefore we have investigated further the scope of this reaction.⁷ Under catalysed conditions at 180°C for 10 h we find that aniline and 1-hexylamine undergo condensation reactions with both cyclic and acyclic alcohols and ketones [eq. (4)].

and secondary amines (Table 6), secondary alcohols and both primary and secondary amines (Table 7), and ketones and primary amines (Table 8). The data in Tables 6–8 show no particular pattern. For the terminal alcohols we only observe significant redistribution products when dipropylamine is used. In addition to the product RNPr₂, the amines R_2NPr , NPr_3 and RNHPr ($R = C_{10}H_{21}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$) are formed in varying amounts depending on the alcohol ROH (Table 6). Similar results are found when secondary alcohols are used (Table 7). For the case of ketones we observe no amine redistribution products when the reaction is



 $(R = H,Me; R' = R'' = C_2H_5; R' = CH_3, R'' = Ph; R' = 1-C_6H_{13}, R'' = CH_3; R''' = Ph, 1-C_6H_{13})$

The yields of product amine are generally low (Table 4), especially for the case where a secondary amine reactant is employed.

In the catalysed condensation reactions of aniline with both 3-pentanone and acetophenone, the respective yields of 3-pentylphenylamine and acetophenyl phenylamine are increased by approximately four-fold when the reaction is carried out under a pressure of hydrogen.⁸ For the case of secondary amines and ketones the yield of tertiary amine is very low even when the catalyst is composed of RuCl₂(PPh₃)₃ with 4 moles of triphenylcarried out in the absence of hydrogen, when the amine yield is very low. Under a pressure of hydrogen the yield of amine is increased, and redistribution products are observed (Table 8).

DISCUSSION

The complex $RuCl_2(PPh_3)_3$ acts as a homogeneous catalyst for the condensation of terminal alcohols with secondary amines to give tertiary amines. At the end of the 2.5 h reaction time the complex has been converted completely into

Table 3. Conversion of 1-decyl alcohol and dipropyl-
amine into decyldipropylamine both in the absence and
presence of triphenylphosphine ⁴

Time	Yield of C_{10} H	$H_{21}NPr_{2}(\%)$
(m)	No PPh ₃	PPh ₃
0	0	0
15	0	0
30	0.1	0.86
45	0.25	5.53
60	0.60	7.78
75	1.65	20.80
90	16.82	21.60
105	18.30	35.10
120	19.70	39.00
135	20.80	47.70
150	24.50	50.60
180	27.00	56.20

^{*a*} Reaction conditions: 3 h at 120°C; 1.00×10^{-2} moles of 1-decyl alcohol and 1.00×10^{-2} moles of dipropylamine; 5.22×10^{-5} moles of RuCl₂(PPh₃)₃ and 2.08×10^{-4} moles of PPh₃.

 $RuHCl(CO)(amine)(PPh_3)_2$. Separate experiments with $RuHCl(CO)(PPh_3)_3$ and secondary amine verify that this complex is not itself a catalyst for the condensation reaction. The initial step of the

reaction apparently results in the formation of an intermediate alkoxide complex which can undergo β -hydrogen transfer to give an aldehydic intermediate. In the presence of excess secondary amine we do not detect any aldehydic intermediates because of their rapid condensation with amine. Two pieces of evidence support the postulate that intermediate aldehydes are formed. The first supportive evidence is the formation of both $RuHCl(CO)L(PPh_3)_2$ (L = amine) and small quantities of alkane in the catalytic reaction. Well-documented examples exist which show that aldehydes are decarbonylated by platinum metal group complexes to give alkanes and carbonyl metal complexes.⁹ The second support comes from a series of separate catalysed and uncatalysed reactions between butyraldehyde and diethylamine at 120°C for 2.5 h reaction time (Table 9). In the absence of catalyst the products of the reaction are the eneal, $CH_3(CH_2)_2CH = C(C_2H_5)CHO$, and the eneamine, $CH_3CH_2CH = CHN(C_2H_5)_2$, in a 44: 1 ratio. In the presence of $RuCl_2(PPh_3)_3$ the products are the eneal and tertiary amine, $(C_4H_9)N(C_2H_5)_2$, in a 8.9 : 1 ratio. In the presence of hydrogen under a pressure of 1300 psig the catalytic reaction is selective for $(C_4H_9)N(C_2H_5)_2$. These results can be explained by eq. (5)

 Table 4. Conversion of ketones and primary or secondary amines into secondary or tertiary amines both in the absence and presence of hydrogen

Ketone	Primary amine	Secondary amine	Yield (%) ^a	Yield (%) ^b
$\overline{(C_2H_5)_2CO}$	PhNH ₂	(C ₂ H ₅) ₂ CHNHPh	5	21
CH ₃ COPh	PhNH ₂	CH ₃ (Ph)CHNHPh	5	23
1-C ₆ H ₁₃ COCH ₃	$1-C_6H_{13}NH_2$	$CH_3(1-C_6H_{13})CHNHC_6H_{13}$	5	50
1-C ₆ H ₁₃ COCH ₃	PhNH ₂	CH ₃ (1-C ₆ H ₁₃)CHNHPh	9	35
0	$1-C_6H_{13}NH_2$	NHC ₆ H ₁₃ ·1	7	31
0	PhNH ₂	NHPh	8	25
ОСН3	PhNH ₂	H _a C	6	25
$(C_2H_5)_2CO$	NHPr ₂	$((C_2H_5)_2CH)Pr_2N$	0	5°
CH ₃ COPh	NHPr ₂	(CH ₃ CHPh)Pr ₂ N	0	4 ^c

"Reaction conditions are 180°C for 10 h with RuCl₂(PPh₃)₃.

^b Reaction conditions are 180°C for 10 h with RuCl₂(PPh₃)₃ and 1300 psig hydrogen.

^c Conditions as for 2 but with 4 moles of triphenylphosphine added.

Ketone	Secondary amine	Tertiary amine	Yield (%)
$(C_2H_5)_2CO$	NHPr ₂	(C ₂ H ₅) ₂ CHNPr ₂	5
CH ₃ COPh	NHPr ₂	CH ₃ (Ph)CHNPr ₂	4
(CH ₃) ₂ CO	$NH(CH_2)_4$	$(CH_3)_2 CHN(CH_2)_4$	5
0	NHPr ₂	NPr ₂	5
1-C ₆ H ₁₃ COCH ₃	NHPr ₂	CH ₃ (1-C ₆ H ₁₃)CHNPr ₂	6
$(C_{2}H_{5})_{2}CO$	$NH(CH_2)_4$	$(C_2H_5)_2CHN(CH_2)_4$	6

Table 5. Conversion of ketones and secondary amines into tertiary amines

Reaction conditions: 10 h at 180° C with RuCl₂(PPh₃)₃ and 4 moles of PPh₃ under a hydrogen pressure of 1300 psig.

 Table 6. Redistribution amine products from the catalytic reaction between terminal alcohols and secondary amines^a

Alcohol	Amine	RNPr ₂	R ₂ NPr	NPr ₃	RNHPr
C ₁₀ H ₂₁ OH	NHPr ₂	63	3	6	
C ₁₄ H ₂₉ OH	NHPr ₂	23	2	3	6
C ₁₆ H ₃₃ OH	NHPr ₂	24		8	11
C ₁₈ H ₃₇ OH	NHPr ₂	21	_	1	

^{*a*} Reaction conditions : 2.5 h at 120°C with RuCl₂(PPh₃)₃. ^{*b*} R = $C_{10}H_{21}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $C_{18}H_{37}$.

	Amine						
Alcohol (ROH)	$(R'NH_2)$	RNHR′	R ₂ NR′	RNR' ₂	R'2NH	R ₂ NH	R' ₃ N
но СН3	PhNH ₂	43	7		_	_	
HO CH3	$1-C_6H_{13}NH_2$	22	13	25	7	5	12
$2 - C_8 H_{17} O H$	$1-C_{6}H_{13}NH_{2}$	33	_		_		6
2-C ₈ H ₁₇ OH	PhNH ₂	18		—	—	—	—
но	$1-C_6H_{13}NH_2$	21	3	and the second	_	—	
2-C ₅ H ₁₁ OH	$1-C_{6}H_{13}NH_{2}$		_	5	—		—
Alcohol (ROH)	Amine (R' ₂ NH)		RNR'2	RNHR′	$\mathbf{R}'_{3}\mathbf{N}$	RNH ₂	
(CH ₃) ₂ CHOH	NHPr ₂		_	_	30		-
но	NHPr ₂	—	13	14	35	—	—
2-C ₈ H ₁₇ OH	NHPr ₂	—	—	—	4		—
но	NHPr ₂	_	14	—	6		_

Table 7. Reaction of secondary alcohols with primary and secondary amines^a

"Reaction conditions: 10 h at 180°C with RuCl₂(PPh₃)₃.

	Product amines (%) ^b							
Ketone (RR'CO)	Amine $(\mathbf{R}''\mathbf{NH}_2)$	Α	В	С	D	Е	F	
(CH ₃ CH ₂) ₂ CO	1-C ₆ H ₁₃ NH ₂	13				12	8	
$(CH_3CH_2)_2CO$	PhNH ₂	21			—		—	
CH ₃ COPh	$1-C_{6}H_{13}NH_{2}$	26	21	13	—		5	
CH ₃ COPh	PhNH ₂	23				0.5		
I-C ₆ H ₁₃ COCH ₃	$1-C_{6}H_{13}NH_{2}$	50			5		_	
1-C ₆ H ₁₃ COCH ₃	PhNH ₂	35	_	—	_	_	_	
	$1-C_{6}H_{13}NH_{2}$	31	—	_	2	1		
	PhNH ₂	25	_		4	—		
Me	PhNH ₂	25	-		4	_	—	

Table 8. Redistribution products from the reaction of ketones with primary amines," RuCl₂(PPh₃)₃, with 4 moles of PPh₃ and 1300 psig hydrogen

"Reaction conditions: 10 h at 180°C with 4 moles of PPh₃ and 1300 psig hydrogen added.

^{*b*} A = (RR'CH)NHR", B = (RR'CH)₂NH, C = (RR'CH)₂NR", D = (RR'CH) NR", E = $R_2^{"}$ NH, F = $R_3^{"}$ N.

whereby the condensation reaction to eneamine is in competition with the self-condensation of the aldehyde to give the aldol eneal product. The formation of saturated amine results from the function of $RuCl_2(PPh_3)_3$ as a hydrogenation catalyst for the intermediate eneamine, and the hydrogenation step is accelerated under hydrogen pressure.

At 120°C for 2.5 h we do not observe any catalysed condensation reaction between dipropylamine and secondary or tertiary alcohols. This



Table 9. Reaction products from butyraldehyde and diethylamine

[&]quot;Conditions are 120°C for 2.5 h.

observation may be due to the failure of $RuCl_2$ (PPh₃)₃ to catalyse either the dehydrogenation of secondary alcohols to ketones or the hydrogenative condensation of ketones with the secondary amine. Under conditions with $RuCl_2(PPh_3)_3$ for 10 h at 180°C we detect *no* tertiary amine formation with 3-pentanone and dipropylamine, diethylamine or pyrrolidine, or with acetophenone and dipropylamine. Furthermore when the alcohol is 2-octanol, 3-pentanol or cyclohexanol we detect no ketone formation.

The data in Table 2 show that $RuCl_2(PPh_3)_3$, but not $RuCl_2(dppe)_2$, $RuCl_2(PN)_2$ (PN = 2-diphenylphosphino-N,N-dimethylaniline) or RuCl₂(bipy)₂, is a homogeneous catalyst for the condensation reaction between terminal alcohols and secondary amines. The difference between $RuCl_2(PPh_3)_3$ and the other complexes is that $RuCl_2(PPh_3)_3$ is a 16-electron complex, whereas the other complexes have 18-electron configurations. The failure of $RuCl_2(PN)_2$ to catalyse the formation of tertiary amines implies that under our experimental conditions the ligand is not hemilabile, whereby the dimethylamino moiety hinges away from the metal centre to create a vacant coordination site.⁵ Adding tin(II) chloride to RuCl₂(PPh₃)₃ does not increase its catalytic activity by introducing $SnCl_3^-$ as a good leaving ligand. Adding triphenylphosphine causes an increase in

catalytic activity of RuCl₂(PPh₃)₃ Triphenylphosphine itself is inactive as a homogeneous catalyst for reaction (1). From the data in Table 3 it is unclear as to the precise function of triphenylphosphine in accelerating the formation of tertiary amines. Since we observe the formation of $RuHCl(CO)(NHPr_2)(PPh_3)_2$ at an earlier stage of the reaction than we do in the absence of triphenylphosphine, it appears that the complete catalytic cycle has been accelerated. Several possibilities can be excluded or considered unlikely. One of these is that chloride ion is replaced by triphenylphosphine to give a catalytically more reactive cationic ruthenium(II) complex. We have eliminated this possibility because solutions of RuCl₂(PPh₃)₃ show no increased conductivity upon addition of excess triphenylphosphine. A second possibility is that triphenylphosphine acts to extend the catalyst lifetime of $RuCl_2(PPh_3)_3$; this postulate is disfavoured by the observation that the catalytically inactive complex RuHCl(CO)NHPr₂(PPh₃)₂ is formed at shorter reaction times in the presence of added triphenylphospine than is found in comparable catalytic runs in its absence.

The proposed catalytic pathway for the condensation reaction between terminal alcohols and secondary amines is shown in Scheme 1. In this scheme a key step is the Schiff base condensation reaction between secondary amine and the inter-



 $RuCl_2P_x(RCH_2NH_2)$



mediate aldehyde formed by β -hydrogen transfer. The tertiary amine product is then obtained by the catalysed hydrogenation of the imine formed in this Schiff base condensation. Two plausible explanations for the accelerating effect of triphenyl-phosphine are that it displaces the complexed aldehyde ligand to facilitate its reaction in the free state with secondary amine, or that it functions to accelerate the catalytic hydrogenation of imine to tertiary amine.

The condensation reaction between ketones and amines under catalytic conditions with $RuCl_2$ (PPh₃)₃ requires a higher temperature than does the condensation reaction between primary alcohols and amines. The primary product is the secondary amine, and the yield is increased under a pressure of hydrogen [eq. (6)].

$$R_2CO + R'NH_2 + H_2 \longrightarrow R_2CHNHR' + H_2O$$
(6)

For secondary amines as reactants, tertiary amines are not formed in the absence of hydrogen, and even under 1300 psig hydrogen pressure the yields are very low [eq. (7)].

$$\mathbf{R}_{2}\mathbf{CO} + \mathbf{R}_{2}'\mathbf{NH} + \mathbf{H}_{2} \longrightarrow \mathbf{R}_{2}\mathbf{CHNR}_{2}' + \mathbf{H}_{2}\mathbf{O} \quad (7)$$

These results support a pathway whereby the final amine is produced by catalytic hydrogenation of an intermediate imine formed in an equilibrium condensation reaction between the ketone and reactant amine [eq. (8)].

$$R_{2}CO + R'NH_{2} \xleftarrow[H_{2}O]{H_{2}O}$$

$$R_{2}C = NR' \xrightarrow[H_{2}]{H_{2}O} R_{3}CHNHR' \quad (8)$$

We propose that the catalytic activity of $RuCl_2$ (PPh₃)₃ results from its functioning as a hydrogenation catalyst for the intermediate imine. This imine is formed in equilibrium with the ketone and amine, and its catalysed hydrogenation to the product amine drives the equilibrium away from the reactant.

The amine redistribution reaction results in decreased selectivity of the catalysed condensation reactions between amines and either alcohols or ketones. These side products cannot be eliminated from the product because this redistribution reaction occurs subsequent to the formation of the initial amine product. Previous researchers have found that these redistribution reactions are catalysed by a series of different ruthenium complexes.¹⁰ The pathway used to explain these reactions is shown in Scheme 2.

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