Cyclopentadienyl Ru^{II} Complexes as Highly Efficient Catalysts for the *N*-Methylation of Alkylamines by Methanol

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The ruthenium(II) half-sandwich complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**) catalyses the reaction between methanol and alkylamines RNH_2 or R^1R^2NH to afford $RN(CH_3)_2$ and $R^1R^2NCH_3$ products, respectively. The reaction is quantitative and generally fast, at the methanol reflux temperature, for a wide spectrum of substrates. Starting from primary amines, the stepwise formation of $RN{=}CH_2$, $RNHCH_3$, and $RN(CH_3)_2$ has been observed. Both PPh_3 and Cl^- dissociation from **1** are key-steps in forming the effective catalytic species. The catalytic activity of several half-sandwich neutral or cationic complexes (**2**–**15**) related to **1** is also discussed.

Introduction

The efficient *N*-alkylation of primary or secondary amines by alcohols is an important synthetic route, the main advantage of which is that water is the only side-product. Thus, the reaction between amines and alcohols has been investigated in detail, particularly using homogeneous catalysts based on late transition metals;[1−12] those based on ruthenium have been the most widely investigated, including the ruthenium(II) complexes [$RuCl_2(PPh_3)_3$],[1,3,5−12] [$RuH_2(PPh_3)_4$],[2,4,5−7] [$RuHCl(CO)(PPh_3)_3$],[5,11] [$RuBr_2(PPh_3)_3$],[6] [$RuHCl(PPh_3)_3$],[6] [$RuH_2\{P(OEt)_3\}_4$],[7] [$RuCl_2(CO)_2(PPh_3)_2$],[8] [$RuCl_2(P{-}N)_2$],[8] (P−N = *o*-diphenylphosphanyl-*N*,*N*-dimethylaniline) [$RuH_2(CO)(PPh_3)_3$],[11] [$\{RuCl_2(\eta^5\text{-}C_5Me_5)\}_2$],[11] as well as those bearing terdentate NPN or NN′N type ligands,[12] the ruthenium(0) derivatives [$Ru(CO)_3(PPh_3)_2$],[5] [$Ru_3(CO)_{12}$],[11] and [Ru(cot)(cod)],[11] and, finally, "in situ" generated systems [$RuCl_3$/phosphane[6,7] or $RuCl_3/P(OR)_3$[6,7]] exhibit catalytic activity in the *N*-alkylation of amines by alcohols. Although the reaction is commonly performed in an autoclave at 120−215 °C, long reaction times are often required to obtain high yields of products.

During our studies[13−18] on the catalytic potential of the half-sandwich ruthenium(II) complex [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**), we found evidence that this readily available compound efficiently catalyses the *N*-methylation of both primary and secondary alkylamines by methanol, under milder conditions than previously reported for other ruthenium systems. Owing to the promising preliminary results obtained with **1**, we extended the investigation to a broad spectrum of half-sandwich ruthenium(II) complexes. In addition, as the *N*-alkylation of amines by alcohols is thought to proceed via an imine intermediate, which is then reduced to amine by a transfer hydrogenation process, useful information on the reduction of the C=N bond by transfer hydrogenation, a process of considerable importance, could also be obtained. The reduction of an imine intermediate is also a key-step in the reductive amination of aldehydes.

The results reported here demonstrate that complex **1** is the most active catalyst so far for the *N*-methylation of alkylamines by methanol.

Results and Discussion

N-Methylation of Amines

The amines employed in this work are shown in Table 1. When a primary (RNH_2) or secondary (R_2NH) alkylamine was refluxed in methanol in the absence of any catalyst, no *N*-methyl derivatives were observed. By contrast, when complex **1** was added to the boiling reaction mixture, the products $RN(CH_3)_2$ and R_2NCH_3, respectively, were quantitatively formed with rates that strongly depend on the nature of the R group. The reactions were carried out, under an argon atmosphere, with 1 mol % catalyst based on amine charged and methanol as solvent at reflux (oil bath 100 °C), with a methanol/amine molar ratio of ca. 100. Under the same experimental conditions, arylamines did not react over a 24 h period. Also, 1,2-ethylendiamine did not react with methanol, most probably owing to its chelation to the metal centre with formation of a catalytically inactive complex.

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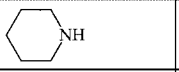
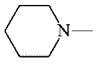
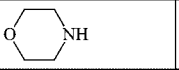
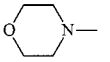
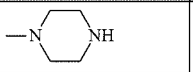
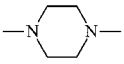
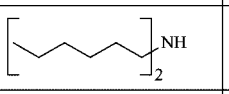
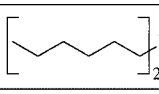
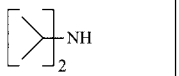
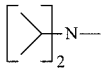
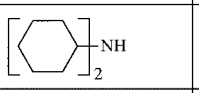
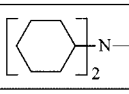
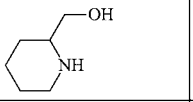
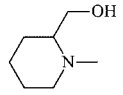
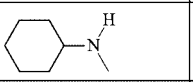
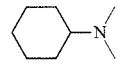
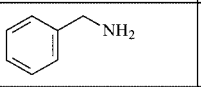
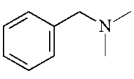
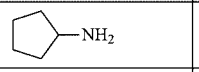
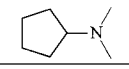
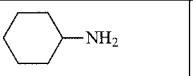
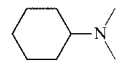
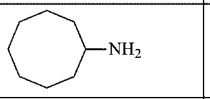
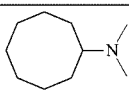
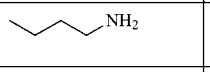
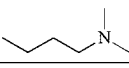
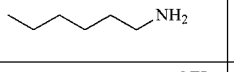
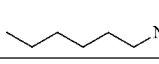
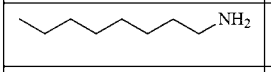
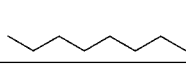
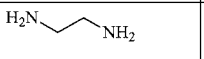
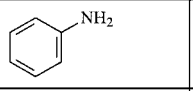
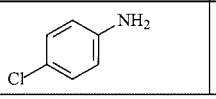
Table 1. Substrates, reaction products and $t_{1/2}$s

Substrate	Product[a]	$t_{1/2}$ [b]
		50 m
		24 h 30 m
		2 h 30 m
		8 h
		4 h 30 m
		7 h
		6 h 30 m
		1 h
		45 h
		2 h 30 m
		2 h 40 m
		3 h
		11 h
		14 h
		21 h
	no reaction	
	no reaction	
	no reaction	

[a] For each substrate the yield is quantitative. Reaction conditions: T = 100 °C, 1 mol % complex **1**, solvent/amine molar ratio ≥ 100. [b] $t_{1/2}$ indicates the time necessary for the consumption of half of the starting amine.

To compare the reactivity of the various substrates, we chose the time needed to consume half of the starting amine ($t_{1/2}$) as a suitable parameter for both primary and secondary amines. The $t_{1/2}$s (Table 1) indicate that both basicity and steric crowding of the starting amine have an important influence on the reaction rate. No clear general trend was found, but the reaction rate usually increases on increasing the basicity of the substrate. For instance, the reaction rate decreased along the series piperidine (2.88), *N*-methylpiperazine (4.15), and morpholine (5.67) (the pK_bs in water solution are in parentheses). Furthermore, benzylamine, which has the highest pK_b (4.67) of the primary alkylamines examined here, shows the highest $t_{1/2}$. Within the series of *n*-alkyl primary amines ($C_xH_{2x+1}NH_2$; x = 4, 6, 8), whose pK_bs are 3.23, 3.44, 3.35 respectively, $t_{1/2}$ increases considerably on going from *n*-butyl- to *n*-octylamine.

To study in detail the *N*-methylation process promoted by **1**, the reaction between methanol and cyclohexylamine (**I**), chosen as a convenient substrate model, has been monitored by GC-MS (Figure 1). Apparently, the reaction proceeds stepwise (Scheme 1), the starting amine **I** being initially transformed into the imine *cyclo*-$C_6H_{11}-N=CH_2$ (**II**), whose concentration remains rather low (ca. 5 %) and almost constant throughout the reaction. A successive hydrogenation process converts **II** into the *N*-monomethyl derivative **III**, which is in turn transformed into the *N*,*N*-dimethyl product **IV**. For this final step, no intermediates could be detected in solution by GC-MS. The total conversion of **I** into **IV** is quantitative within ca. 6.5 h. The subsequent addition of **I** (100-fold excess with respect to **1**) to the reaction mixture requires about 7 h for its complete conversion into **IV**, indicating that the catalytic efficiency of **1** is maintained.

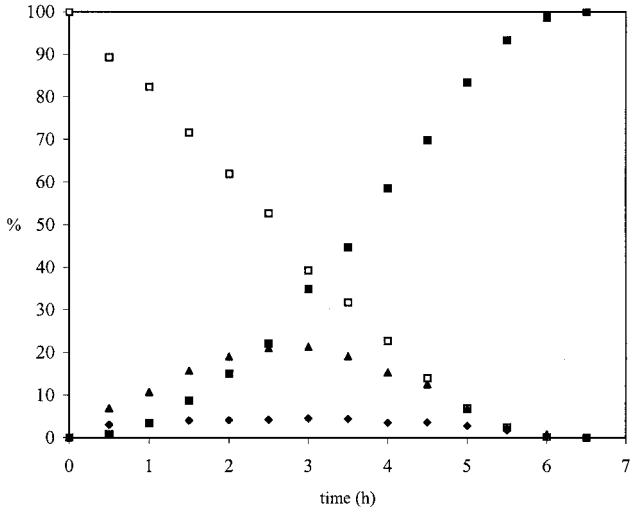
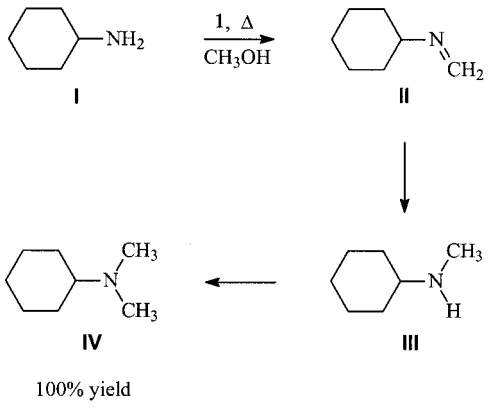


Figure 1. Variation in *cyclo*-$C_6H_{11}NH_2$ **I** (□), *cyclo*-$C_6H_{11}N=CH_2$ **II** (◆), *cyclo*-$C_6H_{11}NHCH_3$ **III** (▲), and *cyclo*-$C_6H_{11}NH(CH_3)_2$ **IV** (■) in the reaction between **I** and CH_3OH, at 100 °C with 1 mol % **1**

The rate of decay of **I** is virtually constant throughout the reaction, and several runs at different initial concentrations of **I** showed that the reaction is zero order for the amine, as reported by Watanabe and co-workers for the reaction between aniline and benzyl alcohol.[5] The effect of reaction time on the methylation of **I** (Figure 1) is similar



Scheme 1. Stepwise formation of *N*,*N*-dimethylcyclohexylamine **IV** from cyclohexylamine **I**

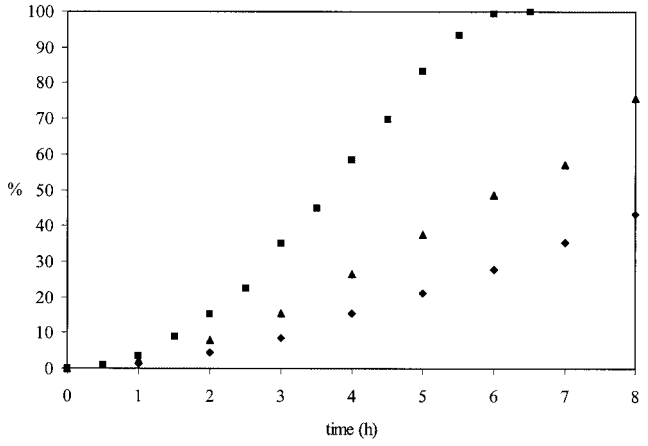


Figure 2. Amount of the product *cyclo*-$C_6H_{11}NH(CH_3)_2$ **IV** in the reaction between *cyclo*-$C_6H_{11}NH_2$ **I** and CH_3OH at 100 °C: with 1 mol % **1** (■); 1 mol % **1** and 5 mol % PPh_3 (▲); 1 mol % **1** and 20 mol % LiCl (◆)

to that reported for the alkylation of aminoarenes with alcohols in the presence of the complexes $[RuCl_2(PPh_3)_3]$[11] and $[RuCl_2(NN'N)(PPh_3)]$[12] {NN′N = $C_5H_3N[CH_2N(CH_3)_2]$-2,6}, for which no imine intermediates were detected in the reaction mixtures.

The reaction has also been carried out in the presence of 0.5 and 2 mol % catalyst, but at higher values complex **1** was not completely soluble in the reaction mixture. With 2 mol % **1**, **I** was converted completely into **IV** within 3.5 h. For the same reaction time 44.7 and 5.9 % of the product **IV** was obtained using 1 and 0.5 mol % catalyst, respectively. A nearly first-order dependence on the initial concentration of **1** was observed. In experiments at 20, 60, 70, and 80 °C, no catalytic activity was shown by **1** at 20 °C, while at 60 °C the reaction proceeded very slowly. At 80 °C the reaction rate was nearly the same as at 100 °C. At 70 °C no appreciable increase of the reaction rate with respect to 60 °C was observed.

Catalytic runs in the presence of different amounts of PPh_3 or Cl^- ions (LiCl) showed that both reagents strongly inhibit the reaction rate. Several experiments were run with PPh_3/**1** or LiCl/**1** molar ratios increasing from 1:1 to 20:1. In Figure 2 are reported the results obtained using a five-fold excess of PPh_3 and a 20-fold excess of LiCl, and, for comparison, that obtained with the catalyst only.

Catalytic Activity of Half-sandwich Complexes

To find the most efficient catalyst, several other half-sandwich ruthenium(II) complexes related to **1** (Table 2) were tested in the model reaction between cyclohexylamine and methanol. The aim was also to better understand the influence of both steric and electronic properties of the ancillary ligands on the catalytic activity of the complexes, and to get more information on the nature of the key-steps occurring at the metal centre.

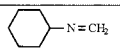
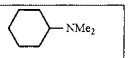
The composition of the reaction mixtures after 6 h (100 °C, 1 mol % catalyst) (Table 2) clearly show that only complex **10**, bearing two P(*m*-Tolyl)$_3$ ligands, exhibits a catalytic activity similar to that of **1**. Complexes **9**, **12**, and **13**, containing the low sterically demanding ligands $PMePh_2$, $PHPh_2$ and CO, and **11** and **14**, bearing bidentate chelating ligands, are much less active than **1**, probably owing to a high activation barrier to neutral ligand dissociation. As regards the effect of the anionic ligand (X), the activity of the complexes decreases in the order **1** (Cl) > **2** (H) > **3** (I) > **4** (N_3) > **5** ($SnCl_3$). This trend apparently depends on both the size of X^- and the strength of the Ru−X bond, which can affect the tendency of half-sandwich ruthenium(II) complexes to dissociate a neutral ligand or the X^- ion to give a coordinatively unsaturated intermediate. Cationic complexes **6**−**8** show a catalytic activity that strongly decreases on increasing the number of coordinated acetonitrile ligands. The very low catalytic activity shown by the indenyl complex **15** is noteworthy since in the redox isomerisation of allyl alcohols to ketones[19b] complex **15** exhibits a higher catalytic activity than **1**, most probably due to the opening of a coordination site on the metal by haptotropic shift (from η^5 to η^3) of the indenyl ligand. Apparently, an analogous behaviour of complex **15** in the *N*-alkylation of amines is not operative.

NMR Measurements and Mechanistic Insights

The transition-metal-catalyzed *N*-alkylation reaction of primary amines with alcohols is generally thought to involve the hydrogenation of an imine intermediate, which results from the condensation of the starting amine with the aldehyde formed by deydrogenation of the alcohol.[1,5,8,11,12] The hydrogen produced in the dehydrogenation process is then transferred to the imine to give the alkylated secondary amine. With secondary amines, the condensation reaction with the aldehyde should give a transient immonium ion.

In the currently accepted mechanism, the ruthenium complex reacts with an alcohol molecule to give, via β-hydride elimination, a Ru−H(aldehyde) intermediate.[1,5,8,11,12] In a second step the condensation product of the aldehyde with the primary amine is hydrogenated by a Ru−H/Ru−H_2 system to the secondary amine. This product can re-enter the catalytic cycle to be converted into a

Table 2. Reaction of *cyclo*-$C_6H_{11}NH_2$ with CH_3OH at 100 °C in the presence of 1 mol % of Ru^{II} complexes **1**−**15**; reaction mixture composition (%) after 6 h[a]

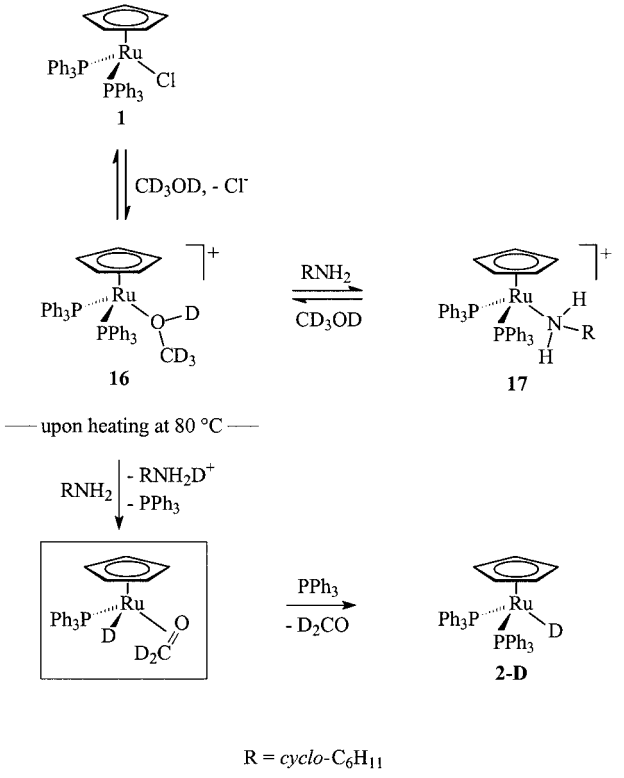
Catalyst	 **I**	 **II**	 **III**	 **IV**
[RuCl(Cp)(PPh_3)$_2$] **1**	0.2	0.3	0.6	98.9
[RuH(Cp)(PPh_3)$_2$] **2**	65.0	5.4	18.9	10.7
[RuI(Cp)(PPh_3)$_2$] **3**	59.5	15.7	18.3	6.5
[Ru(N_3)(Cp)(PPh_3)$_2$] **4**	79.1	5.3	12.5	3.1
[Ru($SnCl_3$)(Cp)(PPh_3)$_2$] **5**	96.8	3.2	0.0	0.0
[Ru(Cp)(CH_3CN)(PPh_3)$_2$]PF_6 **6**	37.6	8.5	20.7	33.2
[Ru(Cp)(CH_3CN)$_2$(PPh_3)]PF_6 **7**	56.1	11.7	17.0	15.2
[Ru(Cp)(CH_3CN)$_3$]PF_6 **8**	92.9	2.7	4.4	0.0
[RuCl(Cp)($PMePh_2$)$_2$] **9**	50.7	4.0	17.8	27.5
[RuCl(Cp){P(*m*-Tolyl)$_3$}$_2$] **10**	0.0	0.6	0.1	99.3
[RuCl(Cp)(dppe)][b] **11**	91.9	3.1	4.5	0.5
[RuCl(Cp)($PHPh_2$)(PPh_3)] **12**	90.0	2.8	7.0	1.2
[RuCl(Cp)(CO)(PPh_3)] **13**	87.6	12.4	0.0	0.0
[Ru(Cp)(Dipy)(PPh_3)]Cl[c] **14**	96.5	3.5	0.0	0.0
[RuCl(Indenyl)(PPh_3)$_2$] **15**	88.0	6.0	4.9	0.4

[a] Cp = η^5-C_5H_5. [b] dppe = 1,2-(diphenylphosphanyl)ethane. [c] dipy = 2,2′-dipyridyl.

tertiary amine. We tentatively propose that a similar mechanism also operates for the *N*-methylation catalysed by **1**.

$^{31}P\{^1H\}$ NMR studies indicate that the dissolution of **1** in CD_3OD occurs with Cl^- dissociation and formation of the cationic solvent complex [Ru(η^5-C_5H_5)(CD_3OD)(PPh_3)$_2$]$^+$ (**16**) (δ = 33.7 ppm). The analogous species containing CH_3OH has been isolated in low yield as the tetraphenylborate salt.[20] Addition of an excess of cyclohexylamine results in the formation of an equilibrium mixture of complexes **1**, **16**, and [Ru(η^5-C_5H_5)(*c*-$C_6H_{11}NH_2$)(PPh_3)$_2$]$^+$ (**17**) (δ = 45.4 ppm). No free PPh_3 is present in solution. Heating at 80 °C causes the catalytic formation of the imine **II** and the amines **III** and **IV**, while free PPh_3 appears in the reaction mixture. At this stage, the formation of the almost catalytically inactive [RuD(η^5-C_5H_5)(PPh_3)$_2$]$^+$ (**2-D**) [1:1:1 triplet, δ = 68.6, $J(^{31}P\text{-}^2H)$ = 4.9 Hz] is also observed (Scheme 2). Complex **17** has been isolated in the solid state in good yield as the perchlorate salt by treatment of complex **1** in THF with a slight excess of $AgClO_4$ in the presence of a tenfold excess of cyclohexylamine. Ru^{II} amino complexes analogous to **17** have been reported previously.[21] The $^{31}P\{^1H\}$ NMR chemical shift of complex **17** agrees with those found in related species with coordinated NH_3 and CH_3NH_2 (δ = 45.9 and 43.7 ppm, respectively).[21b] Prolonged heating of a CD_3OD solution of complex **17** results in its almost complete conversion into **16**.

The RuH(formaldehyde) intermediate, which is most probably the key-species of the catalytic cycle, might reasonably arise from complex **16** via PPh_3 dissociation that



Scheme 2. Complexes detected in solution in CD_3OD on treatment of **1** with excess cyclohexylamine. The species in the square (spectroscopically not detectable) is assumed to be the key-intermediate that initiates the catalytic cycle. Most of **1** is converted into **2-D**, which has a low catalytic activity

provides a vacant coordination site on the metal centre. This hypothesis agrees with the observed decrease in reaction rate in the presence of both free phosphane and chloride ions. In addition, the dissociation of both one PPh_3 and Cl^- from **1** has been previously proposed by Trost to account for the catalytic activity of this complex in other organic transformations.[19]

Finally, we found appreciable amounts of free imine in the reaction mixtures, unlike previous observations in which the imine is formed at the metal centre, by condensation between coordinated amine and aldehyde, and then, without decoordination, immediately hydrogenated to the corresponding amine.[1,5,8,11,12]

Conclusions

Complex **1** is confirmed as a homogeneous catalyst in several organic processes. The results indicate that it, as well as its P(*m*-Tolyl)$_3$ analogue **10**, exhibits the highest reported catalytic activity of ruthenium complexes for the *N*-methylation of primary and secondary alkylamines. Comparison of the literature data on the methylation of different alkylamines by methanol in the presence of Ru-based catalysts with those obtained here (Table 3) shows that **1** promotes a remarkably fast, quantitative conversion, under non-forcing conditions, of the starting amines into *N*-permethylated products. Such good results seem to indicate that complex **1** may also catalyze other organic processes that involve appropriate transformations of alkylamines or imines, such as the hydrogen transfer reduction of the latter.

Experimental Section

Caution! *Perchlorate salts of metal complexes with organic ligands are potentially explosive. These compounds must be handled with caution and should be prepared on a very small scale.*

Instrumentation and Analyses: The NMR spectra (^1H at 200.13, ^{13}C at 50.32, and ^{31}P at 81.02 MHz) in CD_3OD or CD_2Cl_2 solutions were run on a Bruker AC 200 F QNP spectrometer equipped with a variable-temperature probe. The chemical shifts were referenced to internal $SiMe_4$ for ^1H, residual $CHDCl_2$ for ^{13}C, and external 85 % H_3PO_4 for ^{31}P. High temperatures were calibrated with ethylene glycol 80 % in [D_6]DMSO. The GC-MS analyses were carried out with a Fisons TRIO 2000 gas chromatograph-mass spectrometer working in the positive ion 70 eV electron impact mode. The injector was kept at 250 °C and the column (Supelco® SE-54, 30 m long, 0.25 mm i.d., coated with a 0.5 μm phenyl methyl silicone film) was temperature programmed from 50 to 310 °C at 10 °C/min. GC analyses were run on a Fisons GC 8000 Series gas chromatograph equipped with a Supelco® PTA-5 column [30 m long, 0.53 mm i.d., coated with a 3.0 μm poly(5 % diphenyl/95 % dimethylsiloxane) film]; injector and column temperatures as indicated above.

Reagents and Catalysts: All amines (97−99.5 % purity) were purchased from Aldrich and used without further purification. Commercial methanol (Riedel) was purified on CaH_2 according to a standard method[22] and freshly distilled before use. However, the use of untreated solvent resulted in a negligible lowering of the reaction rate. The complexes [RuCl(η^5-C_5H_5)(PPh_3)$_2$] (**1**),[23] [RuH(η^5-C_5H_5)(PPh_3)$_2$] (**2**),[24] [RuI(η^5-C_5H_5)(PPh_3)$_2$] (**3**),[25] [RuN_3(η^5-C_5H_5)(PPh_3)$_2$] (**4**),[25] [Ru($SnCl_3$)(η^5-C_5H_5)(PPh_3)$_2$] (**5**),[26] [Ru(η^5-C_5H_5)(CH_3CN)(PPh_3)$_2$]PF_6 (**6**),[26] [Ru(η^5-C_5H_5)(CH_3CN)$_2$(PPh_3)]PF_6 (**7**),[27] [Ru(η^5-C_5H_5)(CH_3CN)$_3$]PF_6 (**8**),[28] [RuCl(η^5-C_5H_5)($PMePh_2$)$_2$] (**9**),[29] [RuCl(η^5-C_5H_5){P(*m*-Tolyl)$_3$}$_2$] (**10**),[15] [RuCl(η^5-C_5H_5)(dppe)] (**11**),[30] [RuCl(η^5-C_5H_5)($PHPh_2$)(PPh_3)] (**12**),[31] [RuCl(η^5-C_5H_5)(CO)(PPh_3)] (**13**),[32] [Ru(η^5-C_5H_5)(2,2′-dipyridyl)]Cl (**14**),[33] and [RuCl(Indenyl)(PPh_3)$_2$] (**15**)[34] were synthesised according to literature procedures.

Synthesis of Complex [Ru(η^5-C_5H_5)(*c*-$C_6H_{11}NH_2$)(PPh_3)$_2$]ClO_4 (17): Under an argon atmosphere, a mixture of complex **1** (181 mg, 0.25 mmol), $AgClO_4$ (62 mg, 0.30 mmol) and cyclohexylamine (248 mg, 2.5 mmol) was stirred in anhydrous THF (15 mL) for 30 min at room temperature. The resultant mixture was filtered through a glass-frit and then through a Celite® bed to eliminate traces of silver and silver compounds. *n*-Hexane (20 mL) was subsequently added to the solution and the THF pumped off. A yellow−green gum was obtained, which was slowly converted into a yellow solid by vigorous stirring in an ice-bath. The solid was recrystallised from THF/*n*-hexane in 73 % yield (162 mg).

Table 3. *N*-methylation of amines by methanol catalysed by ruthenium-based compounds. Comparison between literature data and the results herein reported[a]

Catalyst (mol %)	Starting amine	Product	Temperature	Time (h)	Yield (%)	Ref.
[$RuH_2(PPh_3)_4$] (5)			Reflux	48	15	[3]
[$RuCl_2(PPh_3)_3$] (1.3)			180 °C	7	95	[4]
$RuCl_3 \cdot nH_2O$ (2)			180 °C	15	3[a]	[8]
[RuCl(η^5-C_5H_5)(PPh_3)$_2$] (1)			100 °C	6.5	100	This work
[RuCl(η^5-C_5H_5)(PPh_3)$_2$] (1)			100 °C	3	100	This work

[a]14 % methylcyclohexylamine was also obtained. [b] 12 % *N*-methylaniline also obtained. [c] 6 % *N*-methylaniline also obtained. [d] cot = η^2-cyclooctene; cod = η^4-1,5-cyclooctadiene.

$C_{47}H_{48}ClNO_4PRu$ (889.37): calcd. (%) C 63.47, H 5.44, N 1.57; found C 63.11, H 5.35, N 1.49 %. $^{31}P\{^1H\}$ NMR (CD_3OD): δ = 45.4 (s); $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ = 43.9 (s) ppm. ^1H NMR (CD_2Cl_2): δ = 0.60−2.32 (m, 11 H, *c*-C_6H_{11}), 4.39 (s, 5 H, C_5H_5), 6.88−7.71 (m, 30 H, C_6H_5) ppm. $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 24.4 (s), 25.2 (s), 34.9 (s), 61.4(t) J(^{13}C-^{31}P) = 2.3 Hz (*c*-C_6H_{11}), 80.6 (t) J(^{13}C-^{31}P) = 2.0 Hz (C_5H_5), 129.3 (*pseudo*-t), 131.0 (s), 133.7 (*pseudo*-t), 135.3 (*pseudo*-quintet) (C_6H_5) ppm.

General Procedure for the Catalytic *N*-Methylation of Amines: A 3-necked round-bottom flask (50 mL), equipped with a condenser and a rubber septum, was charged with catalyst (18.1 mg, $2.5 \cdot 10^{-2}$ mmol). Under an argon atmosphere, amine (2.5 mmol) and CH_3OH (10 mL, ca. 0.25 mol) were then added. After placing the flask in an oil-bath at a controlled temperature (60−100 °C) the initial orange mixture immediately turned into a clean yellow solution. Samples were extracted through the rubber septum with a syringe, diluted with diethyl ether and analysed by GC or GC-MS.

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